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ON CERTAIN SUBSTITUTED ACRYLIC AND PRO-
PIONIC ACIDS.

By Charles F. Mabery.

Bromtrichlorpropionic Acid.[1]— Chlorine unites readily with
chlorbromacrylic acid, and when the reaction is conducted in a
chloroform solution it is attended with the evolution of consider-
able heat. The best results are obtained, as regards both the
purity and the yield of the addition-product, when the solution is
kept cold and exposed to direct sunlight. In three or four hours
the formation of the addition-product is complete, and upon evap-
oration of the chloroform it is left in the form of a crystalline solid
that is easily purified by two or three crystallisations from carbonic
disulphide. In one experiment, with the temperature at several
degrees below zero, 6.5 grams chlorbromacrylic acid absorbed in
two hours 1.5 grams chlorine, corresponding to an amount of
bromtrichlorpropionic acid equivalent to ninety per cent. of the
theoretical yield.

In its general character and crystalline form this acid resembles
the other substituted acids of this series. It is somewhat soluble
in water, with small quantities of which it forms an oil readily sol-
uble in ether, alcohol and chloroform. From a hot solution in

[1] In the preparation and study of bromtrichlorpropionic and trichloracrylic acids I have been
successively aided by the late Mr. Wallace J. Meyer and Mr. Perry L. Hobbs, formerly students
in this laboratory.

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carbonic disulphide it separates on cooling in rhombic prisms, which melt at $83°$–$84°$. It decomposes carbonates readily in the cold, with the formation of the corresponding salts, while alkaline hydrates eliminate the elements of hydrobromic acid. The salts of this acid are comparatively unstable ; they are rapidly decomposed when heated, and the silver salt suffers decomposition at ordinary temperatures. The identity of the acid was established by analysis and a study of several of its salts.

I. 0.4204 gram of the substance gave 0.2201 gram CO_2 and 0.0330 gram H_2O.

II. 0.2540 gram of the substance gave 0.5005 gram $AgCl + AgBr$.

	Calculated for $C_3H_2Cl_3BrO_2$.	I. Found.	II.
C	14.04	14.28	...
H	.78	.87	...
$3Cl + Br$	72.71	...	72.57

The following salts were prepared for analysis :

Baric Bromtrichlorpropionate, $Ba(C_3Cl_2BrO_2H)_2$.—At ordinary temperatures the barium salt appears to be perfectly stable, and it may be obtained by neutralising a solution of the acid with baric carbonate and baric hydrate and allowing it to evaporate spontaneously without the application of heat. It is very soluble in water, and it is left upon evaporation as a gummy mass, which becomes solid on standing. The air-dried salt lost nothing in weight over sulphuric acid, although it was rapidly decomposed when heated to $80°$.

0.8894 gram of the salt dried over H_2SO_4 gave 0.3220 gram $BaSO_4$.

	Calculated for $Ba(C_3Cl_3BrO_2H)_2$.	Found.
Ba	21.28	21.13

Calcic Bromtrichlorpropionate, $Ca(C_3Cl_3BrO_2H)_2$.—The calcium salt may be prepared at ordinary temperatures by neutralisation of the acid with calcic carbonate and calcic hydrate. Upon evaporation the salt was deposited in oblique prisms, which were constant in weight over sulphuric acid after drying in the air.

I. 0.6096 gram of the salt dried over H_2SO_4 gave 0.1522 gram $CaSO_4$.

II. 0.5792 gram of the salt gave 0.1426 gram $CaSO_4$.

	Calculated for $Ca(C_3Cl_3BrO_2H)_2$.	I. Found.	II.
Ca	7.30	7.35	7.24

Potassic Bromtrichlorpropionate, $KC_3Cl_3BrO_2H.2H_2O.$ — A neutral solution of the potassium salt may be evaporated at ordinary temperatures without decomposition. From the concentrated solution the salt separates in rhombic plates that are quite soluble in water and easily decomposed by heat. For analysis a constant weight of the air-dried salt was obtained over sulphuric acid.

I. 1.0927 of the air-dried salt lost over H_2SO_4, 0.1142 gram H_2O.

II. 0.7857 of the air-dried salt lost over H_2SO_4, 0.0805 gram H_2O.

III. 0.6986 gram of the anhydrous salt gave 0.2116 gram K_2SO_4.

	Calculated for $KC_3Cl_3BrO_2H_2 2H_2O.$	I.	Found. II.
H_2O	10.89	10.46	10.26

	Calculated for $KC_3Cl_3BrO_2H.$	Found.
K	13.27	13.59

Trichloracrylic Acid.— Trichloracrylic acid is prepared from bromtrichlorpropionic acid by the action of baric hydrate most conveniently, taking a slight excess over the calculated amount and keeping the solution slightly alkaline for one or two days. Upon acidifying the solution with hydrochloric acid and extracting with ether, the acid is left after evaporation of the ether as an oily liquid which soon solidifies. The crude acid is easily purified by crystallisation from carbonic disulphide, in which it is much less soluble cold than hot. It is sparingly soluble in water, with which it forms an oil, and very soluble in alcohol, ether and chloroform. From carbonic disulphide the acid crystallises in rhombic prisms, which resemble closely the forms of tribromacrylic acid. Its melting-point is 76°. The composition of this acid was established by the following analyses :

I. 0.1942 gram of the substance gave, by Carius' method, 0.4783 gram AgCl.

II. 0.3182 gram of the substance gave 0.2362 gram CO_2 and 0.1068 gram H_2O.

	Calculated for $C_3HCl_3O_2.$	I.	Found. II.
Cl	60.70	60.75	...
C	20.51	...	20.24
H	.58	...	.37

The solubility of trichloracrylic acid in cold water was deter-

mined by the method of V. Meyer. After neutralising the saturated solution with baric carbonate and evaporating to dryness, the barium was determined by ignition with sulphuric acid.

I. 3.8442 grams of a solution saturated at 20° gave 0.1580 gram $BaSO_4$.

II. 4.4664 grams of a solution saturated at 20° gave 0.1738 gram $BaSO_4$.

These determinations correspond to the following percentages :

I.	II.
6.19	5.86

Baric Trichloracrylate, $Ba(C_2Cl_3O_2)_2$ $3\frac{1}{2}H_2O$.—A solution of the barium salt prepared by neutralising the acid with baric carbonate, may be evaporated on the steam-bath without decomposition, and the salt separates from a concentrated solution in the form of branching needles with pearly lustre, which are much less soluble in cold than in hot water. The air-dried salt contains three and a half molecules of water, which are given up at 80°.

I. 1.1638 grams of the air-dried salt lost 0.1338 gram H_2O at 80°.

II. 1.2335 grams of the air-dried salt lost 0.1383 gram H_2O at 80°.

III. 0.6194 gram of the air-dried salt lost 0.0686 gram H_2O at 80°.

IV. 1.4194 grams of the air-dried salt lost 0.1582 gram H_2O at 80°.

V. 0.6044 gram of the anhydrous salt gave, by ignition with H_2SO_4, 0.2916 gram $BaSO_4$.

VI. 0.4980 gram of the anhydrous salt gave 0.2372 gram $BaSO_4$.

VII. 0.9452 gram of the anhydrous salt gave 0.4460 gram $BaSO_4$.

	Calculated for $Ba(C_3Cl_3O_2)_2$ $3\frac{1}{2}H_2O$.	I.	II.	Found. III.	IV.
H_2O	11.48	11.53	11.22	11.08	11.14

	Calculated for $Ba(C_3Cl_3O_2)_2$.	V.	Found. VI.	VII.
Ba	28.19	28.36	28.00	27.74

Calcic Trichloracrylate, $Ca(C_3Cl_3O_2)_2$ $3\frac{1}{2}H_2O$.—The calcium salt resembles the barium salt in its solubility in water, although it appears to be somewhat more soluble in the cold. It separates from a concentrated hot solution on cooling in tufts of branching

needles. For analysis, the air-dried salt was heated to a constant weight at 80°.

I. 0.6220 gram of the air-dried salt lost 0.0854 gram H_2O at 80°.

II. 0.6000 gram of the air-dried salt lost 0.0807 gram H_2O at 80°.

III. 0.9238 gram of the air-dried salt lost 0.1279 gram H_2O at 80°.

IV. 0.5026 gram of the anhydrous salt gave 0.1692 gram $CaSO_4$.

	Calculated for $Ca(C_3Cl_3O_2)_3 \frac{1}{2}H_2O$.	I.	Found. II.	III.
H_2O	13.94	13.73	13.45	13.85

	Calculated for $Ca(C_3Cl_3O_2)_2$.	Found.
Ca	10.26	9.90

Potassic Trichloracrylate, $KC_3Cl_3O_2$.—A neutral solution of the potassium salt when concentrated on the steam-bath deposits the salt in the form of irregular plates, which are sparingly soluble in cold water, very soluble in hot. It cannot be heated to 80° without decomposition, and it loses nothing in weight over sulphuric acid after drying by exposure to the air.

1.0159 grams of salt dried over sulphuric acid gave 0.4209 gram K_2SO_4.

	Calculated for $KC_3Cl_3O_2$.	Found.
K	18.60	18.31

Argentic Trichloracrylate, $AgC_3Cl_3O_2$.—The silver salt may be made by the addition of argentic nitrate to an aqueous solution of the acid. It is precipitated in fine felted needles, which are very sparingly soluble in cold water, more soluble in hot, and it may be recrystallised from a hot solution without decomposition.

0.6002 gram of the salt gave 0.3020 gram AgCl.

	Calculated for $AgC_3Cl_3O_2$.	Found.
Ag	38.23	37.90

In a former paper[1] on certain tetrasubstituted propionic acids, by H. B. Hill and myself, it was shown that the addition-product that resulted from the action of chlorine on a-dibromacrylic acid was essentially different in its properties from the product obtained by the addition of bromine to a-dibromacrylic acid. Since there seems to be little doubt that the positions of the halogens in dibrom- and dichloracrylic acids are represented by the formula $CXH=$

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[1] This Journal **3**, 263.

$CX - COOH$, the addition-products of these acids should be identical. It therefore seemed advisable to seek further confirmation of the results described in the above-mentioned paper in a comparison of the products which I found could be obtained by elimination of the elements of hydrobromic acid from these tetrasubstituted propionic acids. This work was carried on with the assistance of Mr. Perry L. Hobbs.

Bromdichloracrylic Acid from a-Dibromdichlorpropionic Acid. The preparation of a-dibromdichlorpropionic acid from dichloracrylic by the addition of bromine was fully described in the paper cited above. When this acid in aqueous solution is treated with baric hydrate in quantity sufficient to complete the reaction $2C_3Br_2Cl_2O_2H_2 + BaO_2H_2 = 2C_3BrCl_2O_2H + BaBr_2 + 2H_2O$, the solution retains its acid character until nearly the calculated amount is added. But since the product, if immediately extracted, proves to contain unaltered dibromdichlorpropionic acid, which renders its purification somewhat difficult, it is better to keep the solution slightly alkaline for twenty-four hours. It may then be acidified, the oil that separates allowed to subside, and the solution extracted with ether. The product is easily purified by crystallisation from carbonic disulphide or from water, since either of these solvents dissolves it more freely hot than cold. This acid is readily soluble in alcohol and ether; less soluble in chloroform and carbonic disulphide. When heated with water it melts before dissolving, but solidifies on cooling. By slow evaporation of an aqueous solution the acid separates in oblique prisms, which melt at 85°. Its composition was determined by analysis.

I. 0.2150 gram of the substance gave 0.4661 gram $AgCl + AgBr$.

II. 0.7352 gram of the substance gave 0.4465 gram CO_2 and 0.0424 gram H_2O.

III. 0.6420 gram of the substance gave 0.3842 gram CO_2 and 0.0775 gram H_2O.

	Calculated for $C_3BrCl_2O_2H$.	I.	Found. II.	III.
$2Cl + Br$	68.64	68.93	...	...
C	16.36	...	16.56	16.32
H	.46	...	.64	1.27

In determining the solubility of this acid in cold water, a solution was made according to the method of V. Meyer, saturated

with baric carbonate, and the barium determined by ignition with sulphuric acid.

I. 3.7883 grams of a solution saturated at 20° gave 0.1030 gram $BaSO_4$.

II. 3.5945 grams of a solution saturated at 20° gave 0.1001 gram $BaSO_4$.

These results correspond to the following percentages:

I.	II.
2.56	2.62

Baric Bromdichloracrylate, $Ba(C_3BrCl_2O_2)_2 3H_2O$.—Upon evaporation of a solution of this salt, prepared by neutralising the acid with baric carbonate, the salt was deposited in rhombic plates, which were much less soluble in cold than in hot water. When dried to a constant weight in the air it lost three molecules of water at 80°.

I. 0.9585 gram of the air-dried salt lost 0.9210 gram H_2O at 80°.
II. 0.9346 gram of the air-dried salt lost 0.9220 gram H_2O at 80°.

	Calculated for $Ba(C_3BrCl_2O_2)_2 3H_2O$.	Found. I.	II.
H_2O	8.58	8.34	8.36

	Calculated for $Ba(C_3BrCl_2O_2)_2$.	Found.
Ba	23.82	23.51

Calcic Bromdichloracrylate, $Ca(C_3BrCl_2O_2)_2 4H_2O$.—This salt was deposited from a concentrated solution in jagged plates, which were quite soluble in water. After drying by exposure to the air, the salt lost four molecules of water when heated to 80°.

I. 0.8334 gram of the air-dried salt lost 0.1054 gram H_2O at 80°.
II. 0.8027 gram of the air-dried salt lost 0.1014 gram H_2O at 80°.

III. 0.7556 gram of the anhydrous salt gave 0.2150 gram $CaSO_4$.

	Calculated for $Ca(C_3BrCl_2O_2)_2 4H_2O$.	I.	Found. II.
H_2O	13.09	12.54	12.63

	Calculated for $Ca(C_3BrCl_2O_2)_2$.	Found.
Ca	8.37	8.32

Potassic Bromdichloracrylate, $KC_3BrCl_2O_2$.—When deposited from a hot solution the potassium salt forms clusters of anhydrous, pearly needles, which are not decomposed when heated to 80°.

1.0234 grams of the salt dried at 80° gave 0.3565 gram K_2SO_4.

	Calculated for $KC_3BrCl_2O_2$.	Found.
K	15.15	15.63

Argentic Bromdichloracrylate, $AgC_3BrCl_2O_2$.—Upon the addition of argentic nitrate to an aqueous solution of the acid, the silver salt forms a bulky precipitate, which is composed of fine needles. The salt is much less soluble in cold than in hot water, and it may be crystallised from a hot solution without decomposition. It is not readily decomposed by the action of light.

0.9247 gram of the salt gave 0.4091 gram AgCl.

	Calculated for $AgC_3BrCl_2O_2$.	Found.
Ag	33.03	33.31

Bromdichloracrylic Acid from β-Dibromdichlorpropionic Acid.
In the formation of β-dibromdichlorpropionic acid from α,β-dibromacrylic, it was found by H. B. Hill and me that, under proper conditions, the addition of chlorine was easily accomplished, and there seemed little probability of a molecular rearrangement during the progress of the reaction. Recent results confirm this conclusion, especially at low temperatures. In one experiment in direct sunlight, with the temperature at —5°, twenty grams dibromacrylic acid absorbed sufficient chlorine in about one hour to form nearly the theoretical amount of the addition-product. The elements of hydrobromic acid are easily abstracted from this acid by baric hydrate, and when the reaction is conducted in a slightly alkaline solution, it is usually complete in twenty-four hours. Upon acidifying the solution, the product in part falls as an oil, and the remainder may be extracted with ether. Evaporation of the ether leaves an oil which solidifies on standing, and it may be easily purified by successive crystallisations from carbonic disulphide. The acid is sparingly soluble in cold carbonic disulphide and chloroform, readily soluble in alcohol and ether. With water it forms an oil that does not solidify at 0°. It melts at 78°–80°, and forms oblique prisms when deposited slowly from a saturated solution in carbonic disulphide. Its composition was shown by the following analyses :

I. 0.2700 gram of the substance gave 0.5828 gram AgCl + AgBr.

II. 0.2099 gram of the substance gave 0.4490 gram AgCl + AgBr.

III. 0.8560 gram of the substance gave 0.5072 gram CO_2 and 0.0973 gram H_2O.

	Calculated for $C_3BrCl_2O_2H$.	I.	Found. II.	III.
$Br + 2Cl$	68.64	68.61	68.00	...
C	16.36	...	...	16.15
H	.46	...	...	1.00

The solubility of the acid in cold water was determined by neutralising a saturated solution with baric carbonate, and determining the barium by ignition with sulphuric acid.

I. 3.2754 grams of a solution saturated at 20° gave 0.1206 gram $BaSO_4$.

II. 4.8832 grams of a solution saturated at 20° gave 0.1793 gram $BaSO_4$.

These results correspond to the percentages:

I.	II.
6.92	6.90

Baric Bromdichloracrylate, $Ba(C_3BrCl_2O_2)_2\,3H_2O.$ — From a saturated hot solution prepared by neutralising the acid with baric carbonate and evaporating, the barium salt separates in rhombic plates, which are more soluble in hot than in cold water.

I. 0.9841 gram of the air-dried salt lost 0.0854 gram H_2O at 80°.

II. 1.1431 grams of the air-dried salt lost 0.0998 gram H_2O at 80°.

III. 0.7350 gram of the air-dried salt lost 0.0649 gram H_2O at 80°.

IV. 0.9226 gram of the anhydrous salt gave 0.3778 gram $BaSO_4$.

V. 0.9650 gram of the anhydrous salt gave 0.3982 gram $BaSO_4$.

	Calculated for $Ba(C_3BrCl_2O_2)_2\,3H_2O.$	I.	Found. II.	III.
H_2O	8.58	8.68	8.71	8.83

	Calculated for $Ba(C_3BrCl_2O_2)_2.$	Found. IV.	V.
Ba	23.82	24.14	24.26

Calcic Bromdichloracrylate, $Ca(C_3BrCl_2O_2)_2\,4H_2O.$ —The calcium salt crystallises from a hot saturated solution in pearly branching needles, which contain four molecules of crystal water when dried in the air.

I. 0.8742 gram of the air-dried salt lost 0.1134 gram H_2O at 80°.

II. 0.5368 gram of the air-dried salt lost 0.1824 gram H_2O at 80°.

III. 0.5368 gram of the anhydrous salt gave 0.1606 gram $CaSO_4$.

	Calculated for $Ca(C_3BrCl_2O_2)_4H_2O$.	Found.	
		I.	II.
H_2O	13.09	12.97	13.32

	Calculated for $Ca(C_3BrCl_2O_2)_2$.	Found.
Ca	8.38	8.79

Potassic Bromdichloracrylate, $KC_3BrCl_2O_2$.—The potassium salt is made by neutralising the acid with potassic carbonate, and it is deposited from a concentrated hot solution in clusters of fine needles which are not decomposed at 80°.

0.7714 gram of the salt dried over H_2SO_4 gave 0.2662 gram K_2SO_4.

	Calculated for $KC_3BrCl_2O_2$.	Found.
K	15.15	15.49

Argentic Bromdichloracrylate, $AgC_3BrCl_2O_2$.—The silver salt is precipitated in masses of fine needles upon the addition of argentic nitrate to a solution of the acid. It may be recrystallised without decomposition from hot water, in which it is freely soluble, and it is not appreciably affected when exposed to the action of light.

I. 0.9945 gram of the salt gave 0.4411 gram AgCl.

II. 0.8611 gram of the salt gave 0.3780 gram AgCl.

	Calculated for $AgC_3BrCl_2O_2$.	Found.	
		I.	II.
Ag	33.03	33.62	33.05

From the results of this examination, it seems that while the salts of these acids present certain similarities in the water of crystallisation, the physical properties of the acids themselves are essentially different. The explanation offered by Beilstein, in the last edition of the Handbuch der organischen Chemie, to account for the difference in properties of a- and β-dibromdichloracrylic acids by assigning to dibrom- and dichloracrylic acids the formula $CX_2 = CH - COOH$, is theoretically satisfactory; but, unfortunately, it is not supported by experimental evidence thus far obtained, which has been fully reviewed.[1] Although the replacement of an atom of bromine by one of chlorine during the addition of chlorine to $a\beta$-dibromacrylic acid seems improbable, it can hardly be regarded as impossible. The replaced atom of bromine would be taken up immediately by chlorine, and the resulting chlorine monobromide might form an addition-product even more readily than chlorine

[1] H. B. Hill, this Journal **4**, 273.

itself. These reactions might give a substituted acrylic acid with the formula $CCl_2 = CBr — COOH$, which is the only form theoretically possible with a structure different from that of the corresponding product given by a,β-dichloracrylic acid.

ON THE COMPOSITION OF CERTAIN PRODUCTS FROM THE COWLES ELECTRICAL FURNACE.

By Charles F. Mabery.

In a paper presented by the Messrs. Cowles and the writer at the meeting of the American Association for the Advancement of Science at Ann Arbor in 1885, an account was given of the application of electricity to the reduction of refractory oxides, and certain products were described which had been taken from the electrical furnace. At the recent meeting of the association at Buffalo, a paper was presented by myself which gave a description of material that had been obtained during the past year. In this paper I propose to give a more precise account of some of these products, together with analytical results which establish their composition.

Reduction of Aluminum from Corundum.

When corundum, mixed with charcoal, is submitted to the action of an electrical current in this furnace, it is immediately fused and reduction of the molten mass proceeds rapidly. The reduced metal is converted into vapor, which in part condenses in the upper layer of charcoal, while no inconsiderable portion is carried out of the furnace by the escaping gases and burns in the air. Analyses of the mixture of carbon and metal where condensation takes place have shown from ten to fifty per cent. of metallic aluminum. Soot collected at the orifices for the escape of the gaseous products usually contains metallic aluminum, sometimes to the extent of ten or twelve per cent. of its weight. If the ore contains silica the reduced silicon unites with the aluminum in variable proportions below ten per cent. of silicon. A similar reduction takes place with clay; the silicon is dissolved in the metallic aluminum

while in the molten state, and solution of the latter in hydro-chloric acid leaves the silicon in the crystalline or graphitic form. The greater portion of the aluminum, however, may be retained within the furnace by conducting the reduction in presence of a metal with a higher specific gravity, such as copper, iron or tin. If copper is added to the charge of ore, it unites with the reduced aluminum in variable proportions, which depend upon the condi-tions of the experiment. The approximate composition of this alloy can be closely estimated by inspection as it is taken from the furnace. Ten per cent. of aluminum forms the well-known bronze, which is malleable, golden yellow in color, and quite hard. An increase of two or three per cent. of aluminum forms an extremely hard, brittle alloy. A· fifteen per cent. product has a shiny lustre, a steel-gray color, and it may easily be reduced to the finest powder. As the percentage of aluminum increases, the product becomes less lustrous and lighter in color.

The composition of the slag that accompanies the reduction of aluminum is somewhat variable. It usually contains calcic alumi-nate, which is formed from the lime with which the charcoal is treated previous to use. When first taken from the furnace it is hard and compact, but upon exposure to the air it soon falls to a fine powder which shows an alkaline reaction. It is always found above the alloy in the furnace, and it is usually free from copper or alloy. Occasionally, when fused corundum is the chief constituent, it has a fine granular structure ; otherwise it presents a crystalline struc-ture, with a shiny vitreous lustre. The following analyses represent the composition of several slags from experiments made under different conditions :

	I.	II.	III.	IV.	V.	VI.
Al_2O_3 (insoluble)	55.3	66.84	...	69	...	...
Al_2O_3 (soluble)$+Al_2\left(\substack{calc. \\ as Al_2}\right)$	21.8	14.2	26.9	11.8	...	...
CaO	3.7	1.44	...	6.77	...	...
Cu	...	3.32	...	1.00	...	...
C (total)	...	...	...	.69	.65	...
C (combined)	...	...	.8	...	...	.7

These slags usually contain metallic aluminum, as shown by evolution of hydrogen with hydrochloric acid or alkaline hydrates. They rarely contain iron, and are usually nearly free from silicon. The percentage of carbon, as given by direct combustion, or by evolution as a hydrocarbon with dilute acids, has not differed

materially from the results in analyses 3, 4, 5 and 6, given above. Since in the products analysed iron was absent, it would seem that the carbon might be present in the form of a carbide of aluminum.[1]

The reduced metals frequently alloy in proportions that form peculiar products. They sometimes show a crystalline structure, are variable in color, between steel-gray and bright yellow, often with a resinous lustre, and semi-transparent. These alloys contain aluminum, copper, silicon and calcium in variable proportions, and upon exposure to the air they fall to a powder. At 100° they decompose water, with the evolution of hydrogen, and impart an alkaline reaction to the solution, probably due to the presence of metallic calcium.[2] Products similar in appearance are formed when tin instead of copper is mixed with the charge of ore. The following results were obtained in analysis of some of these alloys:

	I.	II.	III.	IV.
Cu	26.7	35	20.00	...
Al_2	66.2	53.3	74.32	15.23
Si	5	12.3	2.86	20.55
Ca	2	.2	2.86	...
Sn	...	...	...	49.26

Upon dissolving the alloy in acids, the silicon was left as a crystalline residue, which was converted into the dioxide by fusion with alkaline carbonates and potassic nitrate. In nearly all specimens of this product the presence of nitrogen could be detected by fusion with potassic hydrate, although several quantitative determinations showed only a small fraction of one per cent. of this element.

Reduction of Corundum in Presence of Iron.

Although iron does not ordinarily form alloys with as high a percentage of aluminum as copper, it will retain aluminum to a greater or less extent. A product obtained by smelting corundum with iron has recently attracted considerable attention. It seems to possess valuable properties for foundry purposes, and it is also available for introducing a small percentage of aluminum into

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[1] Various mixtures of aluminum and carbon, as well as the crystalline alloys described above, were first thought to be carbides of aluminum (see Am. Journ. of Science **30**, 310); and it is probable that this compound is formed in limited quantities when the reduction of aluminum is conducted in the absence of other metals.

[2] Before exposure to the air these alloys gave no alkaline reaction with water at ordinary temperatures. Wöhler (Journ. pract. Chemie [2] **26**, 385 and 474) found that an alloy of calcium and aluminum containing 8 per cent. calcium was permanent in air and water.

steel. When taken from the electrical furnace it presents the
appearance of a very hard, fine-grained white iron, and it contains
usually six to ten per cent. of aluminum. Analyses of different
ingots gave the following results :

	I.	II.	III.	IV.	V.
Fe	85.17	85.46	86.04	86	84.0
Al₂	8.02	8.65	9	9.25	10.5
Si	2.36	2.20	2.52	2.35	2.4
C	...	3.77	...	2.41	2.5

The composition of the slag that is formed with the alloy of
aluminum and iron is shown by the following analyses :

	I.	II.
SiO_2	0.78	4.1
Al_2O_3 (insoluble)	0.20	...
CaO	28.5	14.0
Fe	1.5	29.16
$Al_2 + Al_2O_3$ [sol.] (calc. as Al_2)	38	48.70
S	0.5	...
Graphite	5.0	2.60
Combined C	0.9	0.48

Reduction of Silica.

Sand is reduced in the electrical furnace more readily than
corundum. The oxide is first melted, and large masses of fused
quartz may be taken from the furnace if the process is suspended
at the proper stage. Reduction follows immediately after fusion,
and, upon cooling, the reduced silicon assumes the crystalline con-
dition. If copper is mixed with the charge of ore, it dissolves the
silicon in variable proportions below fourteen per cent., which is
the largest amount that has been observed. The addition of a
small percentage of silicon to certain metals produces a marked
increase in their tensile strength. Silicon bronze shows greater
strength than copper, tin bronze, or phosphor bronze. The
greatest strength hitherto assigned to ten per cent. aluminum
bronze is 100,000 pounds per square inch ; by the addition of one
or two per cent. of silicon the strength of this alloy is frequently
increased to 120,000 pounds.

Silicon Monoxide.

The product obtained by reduction of silica in the absence of

metals is usually composed to a greater or less extent of an amorphous substance, greenish yellow, occasionally inclining to deep green in color, with a vitreous lustre. Since it is always found between the unreduced oxide and silicon, its formation would seem to be the result of partial reduction. This inference is confirmed by analysis, although as yet it has been possible to obtain only a small quantity of pure substance, as indicated by the following results :

I. 0.6319 gram of the substance gave 0.8357 gram SiO_2.

II. 0.4225 gram of the substance gave 0.5611 gram SiO_2.

III. 0.4523 gram of the substance gave 0.6198 gram SiO_2.

Calculated for SiO.	Found.		
	I.	II.	III.
100	96.45	98.60	99.88

This substance is attacked by hydrofluoric acid, although apparently less readily than the dioxide. In specimens containing reduced silicon the latter was left untouched after treatment with this acid. The samples selected for analysis left no residue when treated with hydrofluoric acid. It is slowly changed to the dioxide by fusion with a mixture of alkaline carbonates and potassic nitrate, and it was by this method that the results given above were obtained. One determination of its specific gravity gave 2.893 with water at 4°. This value is somewhat higher than the specific gravity of quartz, 2.6–2.66 (Graham, Alte ausführliches Lehrbuch der Chemie). From the method of its formation, the results of analysis, and the properties of this substance, there seems to be little doubt that it is silicon monoxide.

In the analysis of these products I have received valuable aid from my assistants, Messrs. H. L. Paine, A. W. Smith, C. H. Matthiessen, and from Mr. H. N. Yates, analytical chemist to the Cowles Electric Smelting and Aluminum Company.

IX.—AMERICAN BARLEY.

By Clifford Richardson.

Notwithstanding the importance to the brewing interests of this country of an accurate knowledge of the characteristics of our barleys, but few analyses have been made hitherto. These include nine collected by Brewer in his Report to the Tenth Census, and eleven specimens examined at the Brewers' Experiment Station, New York. Abroad more attention has been paid to the subject, especially by Maercker[1] at Halle, who concludes that the production of barley cannot be improved by selection of seed alone. Care in other directions and favorable climatic influences, over which there is no control, are necessary as well. Heavy manuring with nitrogen is most injurious, increasing the albuminoids; and a barley rich in these constituents he has found, from experience, to be poor in quality, while a low content is, as a rule, expressive of high quality, the effects of rain and moisture being excluded. From the weight per bushel but little can be learned, and he decides that little attention should be paid to it. The mealiness of the grain was found, however, to be a most important indication, glassy grain being too rich in albuminoids. In fact, as a whole, the characteristics of a good barley are fine color, mealy consistency and small amount of albuminoids. Accordingly, he grades as follows the crops raised at Halle from certain selected seed which had been cultivated with the intention of improving the grain grown in that vicinity :

Specimens denominated.							Mean percent. of albuminoids.
Extremely fine,	.	.	.	.	.	.	8.09
Fine, .	.	.	.	.	.	.	8.67
Good, .	.	.	.	.	.	.	8.93
Medium,	.	.	.	.	.	.	9.78
Under medium,	.	.	.	.	.	.	10.24

and finds the mealiness of the crop as compared to that of the seed to be, under different conditions of nitrogenous manuring :

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[1] Magdeburgische Zeitung, 1885, 443 and 445 ; Bied. Centbl. f. Agrikulturchemie **13,** 491-2.

	Per Cent. of Mealy Kernels.			
	Saalish.	Danish.	Moravian.	Slavonian.
Seed, ...	80.0 per ct.	90.0 per ct.	90.0 per ct.	92.0 per ct.
100 kilograms saltpetre,	62.4	70.1	68.7	77.5
200 kilograms saltpetre,	64.9	65.9	66.8	64.7
Mean, ...	63.7	68.0	67.8	71.1
Less than seed, . . .	16.3	22.0	22.2	20.9

These results are of interest, and, aside from a knowledge of the percentage of albuminoids in barleys from various sources on the Continent and elsewhere, form the only basis which we have for a study of the character and relative value of this grain, as it is grown in different parts of this country, and matured under the most varied conditions of climate and general environment.

The samples of American barley have been collected from those parts of the country where it is a crop of any prominence. They represent fairly well the production of the United States and Canada, although the harvest in Canada was not quite equal to the average. The largest number of analyses are not for the largest areas of production—New York, Wisconsin and California, which raise more than half the crop—but they are scattered through all the States where any amount of barley is grown. In considering the average features of this cereal as it is found in market, regard must be had especially for the figures for Canada and the three States named, although the California barley reaches our Eastern markets in small amount.

Omitting the analyses in detail, which can be found in our original bulletin, the following are the averages derived from them:

Average Physical Properties of American Barleys.

STATE.	No. of determinations.	Weight per 100 grains.	Weight per bushel.	Mealy.	Half mealy	Quarter mealy	Little mealy	Glassy.
		Grams.	Pounds.					
United States......	76	3.482	54.0	20	35	29	15	1
Canada............	12	3.688	54.7	19	37	29	13	2
Eastern States...................	13	3.016	52.6	11	29	32	26	2
Western States...	39	3.171	52.8	21	35	30	13	1
Northwestern States........	10	3.680	57.2	27	35	26	11	1
Pacific Slope	12	4.655	56.8	21	40	29	10	0
Vermont	3	3.193	52.0	13	24	24	24	5
New York.......................	8	3.217	53.1	11	32	31	26	0
Ohio...........	4	3.230	52.1	33	38	21	8	0
Michigan....	6	3.150	54.0	14	34	34	16	1
Indiana	3	3.330	53.5	28	35	24	13	0
Illinois	5	2.890	51.1	28	32	25	15	0
Wisconsin.......................	5	3.320	51.3	22	30	31	14	3
Minnesota	7	3.290	52.7	22	43	29	6	0
Iowa...........................	7	3.030	53.4	17	34	32	16	1
Dakota.........................	5	3.354	54.2	15	39	32	13	1
Montana........................	5	4.220	59.1	45	28	17	10	0
Nevada.....	2	4.215	55.7	....	....	....	....	1
Oregon.........................	2	4.800	56.1	12	30	40	18	0
California	5	4.900	53.0	26	46	23	5	0

Average Composition of American Barleys (Unhulled) Arranged by States.

STATE.	Number of analyses.	Water.	Ash.	Oil.	Carbohydrates.	Fibre.	Albuminoids.	Nitrogen.
		Per ct	Per ct	Per ct	Per ct	Per ct	Per ct	Per ct
United States......................	60	6.53	2.89	2.68	72.77	3.80	11.33	1.81
Atlantic Slope...................	10	6.64	2.51	2.59	73.02	3.57	11.59	1.85
Northern States................	48	6.55	2.87	2.69	72.55	3.76	11.58	1.85
Western States.................	30	6.66	2.96	2.73	72.26	3.87	11.52	1.84
Northwestern States..........	8	6.62	2.85	2.69	73.03	3.59	11.82	1.89
Pacific Slope..................	10	6.47	3.05	2.65	72.43	3.90	11.50	1.69
Vermont........................	3	6.58	2.51	2.77	71.41	3.84	12.89	2.06
Connecticut....................	1	6.50	2.99	2.33	75.14	2.89	10.15	1.62
New York.......................	5	6.77	2.46	2.65	73.59	3.50	11.03	1.76
Pennsylvania...................	1	6.27	3.05	2.06	72.89	3.83	11.90	1.90
Ohio............................	4	6.68	3.25	2.64	72.95	4.19	10.28	1.64
Michigan........................	5	6.47	2.79	2.72	72.34	3.42	12.46	1.99
Indiana.........................	2	5.95	3.23	3.13	73.28	3.99	10.42	1.67
Illinois........................	4	6.37	3.68	2.67	71.84	3.66	12.38	1.98
Wisconsin.......................	5	7.05	2.95	2.63	71.87	4.05	11.45	1.83
Minnesota.......................	5	7.29	2.63	2.81	72.87	4.01	10.39	1.66
Iowa............................	4	6.27	3.08	2.71	71.37	4.01	12.56	2.01
Nebraska........................	1	7.58	3.00	2.70	71.12	3.35	12.25	1.96
Dakota..........................	5	5.81	2.99	2.77	71.75	3.66	13.02	2.08
Montana.........................	3	6.37	2.62	2.56	75.17	3.48	9.80	1.57
South Carolina.................	1	6.85	2.65	2.45	73.62	4.10	10.33	1.65
Kentucky........................	1	6.00	2.90	2.37	75.73	4.25	8.75	1.40
Utah............................	1	7.70	3.40	2.53	72.99	2.88	10.50	1.68
Arizona.........................	1	6.26	2.90	2.63	74.30	4.28	9.63	1.54
Washington......................	5	5.95	3.50	2.98	70.97	4.35	12.25	1.96
Oregon..........................	2	6.23	2.92	2.38	74.23	3.91	10.33	1.65
California......................	3	5.80	3.30	2.74	74.86	4.25	9.05	1.45
Wyoming.........................	1	6.70	2.20	2.52	74.03	3.00	11.55	1.85
Colorado........................	1	8.15	2.77	2.87	68.99	3.92	13.30	2.13

The examination of the Canadian barleys is given in detail, as they were especially selected as graded specimens of the crop of 1885.

Canadian Barleys.

GRADE.	Serial number.	District.	Composition.							Weight.		Consistency.					
			Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Nitrogen.	Weight per 100 grains.	Weight per bushel	Mealy.	Half mealy.	Quarter mealy.	Little mealy.	Glassy.	
			P.ct.	P.ct.	P.ct.	Per ct	P.ct.	Per ct	P ct	Grms.	Lbs.						
First quality........	6041	A1	7.58	2.98	2.70	73.49	3.10	10.15	1.62	2.910	54.8	16	32	24	20	8	
" "	6044	B1	8.35	2.73	2.69	73.23	3.55	9.45	1.51	3.069	56.1	..	48	36	12	4	
" "	6047	C1	6.95	2.68	2.64	74.28	3.65	9.80	1.57	3.206	55.9	40	28	20	12	..	
" "	6050	D1	8.35	2.88	2.67	73.13	3.69	9.28	1.48	3.445	52.7	12	36	36	16	..	
Average...........			7.81	2.82	2.67	73.53	3.50	9.67	1.54	3.158	54.9	17	36	29	15	3	
Second quality......	6042	A2	7.85	2.95	2.72	72.76	3.22	10.50	1.68	2.818	54.5	36	40	12	12	..	
" "	6045	B2	7.03	2.80	2.80	73.46	3.76	10.15	1.62	3.056	54.7	16	36	28	16	4	
" "	6048	C2	10.08	1.62	2..8	72.58	3.49	9.45	1.51	2.934	53.5	12	36	32	20	..	
" "	6051	D2	8.43	3.18	2.63	72.55	3.41	9.80	1.57	3.257	53.5	24	40	32	4	..	
Average...........			8.35	2.64	2.73	72.84	3.47	9.97	1.59	3.021	54.1	22	38	26	13	1	
Third quality.......	6043	A3	8.78	2.70	2.69	72.35	3.50	9.98	1.60	3.012	52.4	36	28	24	8	4	
" "	6046	B3	6.75	2.83	2.72	73.87	3.68	10.15	1.62	3.094	54.8	16	44	32	..	8	
" "	6049	C3	8.13	3.05	2.67	72.82	3.35	9.98	1.60	2.941	52.4	..	40	44	16	..	
" "	6052	D3	7.93	3.18	2.74	73.47	3.35	9.33	1.49	3.226	54.3	20	32	24	20	4	
Average...........			7.89	2.94	2.71	73.13	3.47	9.86	1.58	3.068	53.5	18	36	31	11	4	
Average A locality			8.07	2.88	2.70	72.87	3.27	10.01	1.63	2.943	53.9	30	33	20	13	4	
Average B locality..			7.3	2.79	2.74	73.52	3.66	9.92	1.58	3.073	55.2	11	43	32	9	5	
Average C locality..			8.39	2.45	2.70	73.23	3.49	9.74	1.56	3.027	53.9	17	35	32	16	..	
Average D locality..			8.24	3.08	2.68	73.05	3.48	9.47	1.51	3.309	53.5	19	36	31	13	1	
Grand average....			8.02	2.80	2.70	73.17	3.48	9.83	1.57	3.088	54.1	19	37	29	13	2	

The districts in which the grain was grown are represented by the letters A, B, C and D, and included: A, the counties north of the central part of Lake Erie; B, the counties north of the north-western part of Lake Ontario; C, the counties north of the central portion of Lake Ontario; D, the counties north of the northeastern portion of Lake Ontario, bordering on the Bay of Quinte.

B, C and D are considered to produce the best barleys, and especially D, the crop of which was, however, unfortunately injured by rain. The brightest grain is found in B.

As this barley forms a great portion of our supply, and is looked upon as the best, it will be considered first, and that of the United States compared with it.

Maercker found that the finest grain contained not more than 8 per cent. of albuminoids, and consisted of at least 80 per cent. of mealy kernels. These two factors, together with the brightness of the grain, he considered to be the characteristics by which its quality should be judged.

Of the twelve typical specimens of the Canadian crop, none were below nine per cent. of albuminoids, the average being 9.83, and only 6 contained 60 per cent. of kernels which were mealy or half mealy in structure. They cannot be said, therefore, to be equal to what is considered extremely fine barley in Germany. They do, however, reach, and in most cases exceed, the average production of foreign countries, and may be considered as of extremely good quality for samples from actual trade lots, and better than those produced the world over. In weight per bushel they are about the same as or slightly heavier than the average found by Maercker—52 pounds—and in moisture, as with all our grain, much dryer than the product of damper climates.

The differences in the different grades are marked almost entirely by brightness and perfection of the kernel, there being a remarkably close agreement in all other respects. This shows how important a factor climate and care in harvesting and handling is in enhancing or depreciating the value of the grain. The latter factor—care—is almost entirely within the control of the farmer, while meteorological conditions, of course, are not, except so far as the all-important point of selection of locality is within his power. Of the different districts, that north of Lake Erie produces the specimens richest in nitrogen, which would therefore be graded lowest as far as this influences our judgment, thus agreeing with

current opinion. In mealiness these specimens are much ahead of all the others, and this ought to more than balance the slightly higher percentage of albuminoids ; but the summer rains eventually, by coloring the grain, have the greatest influence in determining its quality, and make the barley of this district the least desirable. The remaining districts north of Ontario produce grain much alike, that from the B district averaging heavier in weight per bushel, and that from D being a little less nitrogenous. As a whole, these Canadian barleys certainly form a very good standard of reference.

In comparing the barleys of the United States with those of Canada, it appears at once that, as a whole, the former average about as mealy in consistency as the latter. Examined by distribution geographically, the Eastern grain is found to be much less mealy than the Western, that of the Northwest being the richest in mealy kernels. Again, however, we find that but two out of sixty-four samples contained 80 per cent. or over of mealy or half-mealy kernels. In weight per bushel there is no variation from Canadian and foreign grain, but in size the barleys of the United States, as a whole, are larger than those of Canada. Unfortunately, we have no data for those of foreign production. The Eastern grain is no larger than the Canadian, and the average is increased by the large size of that from the Northwest and the Pacific Slope, which, at the same time, has an increased weight per bushel. The high percentage of albuminoids stored up in the peculiar climate of the Northwest, while an advantage in the wheat grain, would be a serious objection in barley. In fact, it appears that the average amount of albuminoids in the barley of the United States is greater than that of Canada, and far ahead of anything which Maercker would consider desirable. California alone is 1 per cent. below the average for the rest of the country, there being less than one-half per cent. difference from 11.50 per cent. in the average for all but California, which has 10.50 per cent. This is higher than was found in the Canadian grain, so that it may safely be said that the latter is at present the best, in so far as this constituent is to be considered as a test of quality.

In brightness, the samples from those portions of the country having a dry climate at harvest-time, especially the Pacific Slope and the Northwest, were far superior. This is an important feature in considering the best areas for the production of good malting barley ; and while California as yet furnishes but little for brewing

purposes, it is without doubt one of our best fields, as with a proper selection of seed and system of cultivation it will not be difficult to reduce the albuminoid constituents to a figure corresponding with the brightness of the grain.

Among the numerous analyses, the following extremes were found:

	Highest per cent.	State.	Lowest per cent.	State.
Water, ...	9.15	Minnesota.	4.53	California.
Ash, ...	4.43	California.	1.50	Minnesota.
Oil, ...	3.54	Indiana.	2.06	Oregon.
Carbhydrates, ...	76.79	Montana.	68.99	Colorado.
Crude fibre, ...	4.65	Ohio.	2.64	Illinois.
Albuminoids, ...	14.88	Dakota.	8.75	Kentucky & Or.
Weight per 100 grains, grams, .	4.900	California.	2.630	Pennsylvania.
Weight per bushel pounds, . .	60.2	Utah.	50.4	Pennsylvania.
Per cent. of mealy and half-mealy kernels, ...	100.00	Montana.	16.0	Vermont.

Dakota sustains its reputation for high nitrogen and Oregon for low, but the variations in this constituent are not as wide as in wheat; barley, and also rye, appearing to be less affected in this respect, although Maercker's experiments show that barley responds in its percentage of albuminoids readily to nitrogenous manuring. His seed was, however, very poor in albuminoids—7.7 to 8.0 per cent.—and would naturally increase when the conditions were made favorable.

In Koenig's collection of analyses of this grain he gives as the average of 127 specimens from all parts of the world:

					Per cent.
Water,	.	.	.	.	. 13.77
Ash,	.	.	.	.	. 2.69
Oil,	.	.	.	.	. 2.16
Carbhydrates,		.	.	.	. 64.93
Crude fibre,	.	. .	.	.	. 5.31
Albuminoids, .		.	.	.	. 11.14
Total, .		.	.	.	. 100.00

This is but little different from the average product of the United States, and would point to the fact that our barley is as good for malting purposes as most of the world's production. Canada, in fact, as shown by the specimens which have been examined from there, is well above foreign averages in starchiness.

Experience and care have taught Canadians, in connection with their favorable climate, the means of producing an excellent grain, superior to other parts of the country. It seems quite possible for the farmers in many portions of the United States, and especially California, the climatic conditions of which are such as to avoid damaging summer rains, with not too dry and hot a climate, to increase our supply of barley of good quality.

There is one condition which in the case of wheat was found to be of evident effect. Although almost all the specimens examined were spring-sown grain, twelve of winter barley were found to contain but 10.05 per cent. of albuminoid, as compared to 11.42 in the spring varieties. Whether this could be made of any importance in practice cannot, of course, be decided except by the possibilities of the culture of winter barleys, which as yet seem to be small.

The greater inferiority of our average product is probably due more to attempts to grow it in localities of unsuitable climatic nature, or lack of care in cultivation, than to any other reason.

In a few samples the outer covering of the grain was detached and weighed—a point of interest to the brewer and malter. The extreme amounts were 16.94 and 12.55 per cent., not nearly as large as in oats. Following are the determinations:

Barley—Percentages of Grain and Hulls.

Number.					Grain. Per cent.	Hull. Per cent.
4015, California,	.	.	.	.	83.06	16.94
4081, Indiana,	.	.	.	.	83.78	16.22
4090, Indiana,	.	.	.	.	83.70	16.30
4097, Iowa, .	.	.	.	.	84.25	15.75
4107, Iowa, .	.	.	.	.	85.72	14.28
4156, Michigan,	.	.	.	.	84.01	15.99
4166, Minnesota,	.	.	.	.	84.47	15.53
4179, Minnesota,	.	.	.	.	86.28	13.72
4202, Nevada,	.	.	.	.	84.93	15.07
4205, Nevada,	·	.	.	.	87.45	12.55
4220, New York,	.	.	.	.	84.96	15.04
Average,	.	.	.	.	84.78	15.22

For many other details reference must be made to the original bulletin, which can be had upon application.

A METHOD FOR THE SEPARATION AND ESTIMA-
TION OF BORIC ACID.

With an Account of a Convenient Form of Apparatus for Quantitative Distillations.

By F. A. Gooch.

In all successful methods for the estimation of boric acid, its comparative isolation is a necessary preliminary. Fortunately, the removal of nearly everything which interferes seriously with the proper execution of methods is not particularly arduous; but, of ordinarily occurring substances, two, silica and alumina—both very commonly associated with boric acid—are especially annoying in this regard. In the separation of alumina the trouble lies in the tendency of the precipitated hydrate to carry and retain boric acid,[1] so that the two cannot be parted by means of ammonia or ammonia salts; with silica, the difficulty is in removing it completely. The volatility of boric acid stands, of course, absolutely in the way of treating with acid and evaporating to dryness, and every chemist knows the vainness of attempting to precipitate silica by means of ammonia, ammonia salts, or zinc oxide in ammonia. In Stromeyer's method[2] the presence of silica is peculiarly harmful, since in passing to the condition of potassium fluosilicate this substance nearly quadruples its weight, and to free the potassium fluoborate from contaminating fluosilicate requires, according to Fresenius,[3] at least six treatments by solution in boiling water, the addition of ammonia, and evaporation to dryness. Wöhler[4] recommends evaporating the hydrochloric acid solution to dryness in a flask fitted to a condenser, collecting the distillate, reuniting the latter with the residue, and filtering from silica; and the operation is successful so far as the complete removal of silica is concerned; but the alumina, if present, is still in condition to give annoyance, and the other bases are yet to be separated.

Advantage has long been taken of the volatility of free boric acid with hydrofluoric acid or with alcohol to secure its removal from fixed substances, but so far as I know no attempt has been made

[1] Wöhler, Ann. d. Chem. u. Pharm. **141**, 268.
[2] Ann. d. Chem. u. Pharm. **100**, 82.
[3] Quant. Chem. Anal. 424.
[4] Handbook of Mineral Analysis, under "Datholite."

heretofore to secure its complete volatilisation and estimation in the distillate. The experiments which I proceed to describe are the result of an effort to accomplish this end.

Aside from the difficulties in manipulation and in the construction of apparatus which the use of hydrofluoric acid would involve, this reagent is otherwise plainly inapplicable to the purpose in view, and of other agents with which boric acid is known to volatilise freely methyl alcohol seems to present the most desirable qualities. Methyl alcohol, ethyl alcohol, and water are effective in the order in which they are named. Thus, to volatilise 1 gram of boric acid —the equivalent, speaking roughly, of about 0.5 gram of boric anhydride—two treatments with 10 cc. of methyl alcohol and evaporation to dryness in each case were adequate ; for the volatilisation of 0.2 gram of boric acid were required two treatments of 10 cc. each of ethyl alcohol, succeeding an evaporation with 50 cc. of the same alcohol ; and the residue of five evaporations of water over 0.4 gram of boric acid, taking in each case 50 cc. of water, followed by ignition, weighed 0.08 gram or one-fifth of the original weight. In the presence of water, methyl alcohol is not equally effective; amyl alcohol and sulphuric acid restrain its action similarly, doubtless by dilution simply, and hydrochloric acid seems to possess no advantage over water alone in developing the volatility of boric acid. As an example, an experiment may serve in which a solution of 0.4 gram of boric acid in 50 cc. of water, after being heated three times successively with 25 cc. of methyl alcohol until the boiling-point rose in every case nearly to that of water, and then evaporated to dryness, left a large residue which disappeared with a single charge of 25 cc. of methyl alcohol applied by itself.

From the residue of the evaporation of borax with hydrochloric, nitric, or acetic acid, methyl alcohol, as would naturally be predicted, volatilises the boric acid freely, though the presence of foreign material acts to a certain degree protectively and tends to diminish the rapidity with which the alcohol would otherwise effect extraction and volatilisation. In case, however, that acetic acid is used to break up the borate, the tendency of sodic acetate to lose acid and become alkaline simply by exposure to evaporation in its aqueous solution makes it necessary to insure the acidity of the residue of evaporation by adding a drop or two of acetic acid before repeating the treatment with methyl alcohol.

On the whole, methyl alcohol shows itself to be an excellent agent by which to secure the volatilisation of boric acid.

To retain free boric acid, magnesium oxide naturally suggests itself. According to Marignac,[1] it is effective, and if, in the course of analysis, it may have been partly converted to the chloride, it is easily regenerated by the action of heat and moisture. Marignac, it will be remembered, makes use of magnesia mixture—the chlorides of ammonium and magnesium with free ammonia—to fix the boric acid, evaporating the solution to dryness, igniting, extracting with boiling water, filtering, and weighing the residue, while the filtrate is again treated as before to recover traces of the borate, which has yielded to the solvent action of the water. During the drying and ignition the magnesium chloride yields hydrochloric acid, and it would seem scarcely possible that the magnesium borate should fail to show some loss of boric acid when both hydrochloric acid and moisture exert their action. Further, the presence of ammonia during evaporation does not prevent the volatilisation of boric acid,[2] and Marignac regards the addition of it from time to time as of doubtful use. So it appears natural to look for some loss under such conditions, and Marignac fully recognises the fact that the apparent accuracy of his method is due to the balancing of errors, the inclusion of foreign matter by the magnesium borate and the deficiency of the magnesia when precipitated as ammonio-magnesium phosphate together compensating for the loss of boric acid by volatilisation. To bring the matter to the test, the following experiments were made. In them and in all succeeding experiments the boric acid was weighed in solution, the standard of this having been fixed by dissolving in a known weight of water a known weight of fused boric anhydride prepared in a state of purity by frequent recrystallisation. The magnesium oxide employed was made from the pure chloride by precipitating by ammonium carbonate and igniting, and was free from lime and alkalies, and, as far as could be determined, otherwise pure. The whole operation of each experiment was conducted in one vessel, so as to avoid transfers. In all cases a weighed platinum crucible of 100 cc. capacity received a weighed portion of magnesia, and after ignition and subsequent weighing the weighed solution of boric acid was introduced. In Experiments (1) to (4) the magnesia was thoroughly stirred in the solution of boric acid, the evapora-

[1] Zeit. für Anal. Chem. **1**, 406.   [2] Rose, Pogg. Ann. **80**, 262.

tion carried at once to dryness, and the crucible and residue ignited and weighed; in Experiments (5) to (8) the magnesia was dissolved, after the addition of the boric acid, in hydrochloric acid sufficient in amount to prevent the precipitation of magnesium hydrate on the subsequent addition of ammonia, ammonia introduced in considerable excess in (7) and (8), in distinct excess in (5) and (6), the whole evaporated and ignited, the residue moistened and again ignited, and this last treatment repeated until the residue ceased to yield vapor of hydrochloric acid when heated.

	B_2O_3 taken.	MgO taken.	$MgO + B_2O_3$ found.	B_2O_3 found.	Error.
	Gram.	Gram.	Gram.	Gram.	Gram.
(1)	0.1734	0.5005	0.6607	0.1602	0.0132—
(2)	0.1804	0.4973	0.6660	0.1687	0.0117—
(3)	0.1793	0.4949	0.6640	0.1691	0.0102—
(4)	0.1794	0.4941	0.6627	0.1686	0.0108—
(5)	0.1807	0.4984	0.6542	0.1558	0.0249—
(6)	0.1789	0.4974	0.6687	0.1560	0.0229—
(7)	0.1806	0.4944	0.6684	0.1740	0.0066—
(8)	0.1789	0.4959	0.6672	0.1713	0.0076—

From these results it appears plain that under the conditions of the experiments neither magnesia alone nor the magnesia mixture is efficient in fixing boric acid; but in Experiments (7) and (8), in which ammonia was employed in large excess, the loss of boric acid is least, so that it would seem to be the case that though ammonia is not a perfect preventive of volatilisation, it does exert a restraining action on the boric acid. That the magnesia mixture should be incapable of retaining entirely the boric acid present is, as has been pointed out, not surprising ; but that the loss should be so great is rather startling, and more than suggests that the errors of Marignac's process are seriously excessive. The failure of magnesium oxide to hold back boric acid under the conditions of the experiment must be due to a cause other than that which determines the loss during the evaporation and ignition of the magnesia mixture, and for this it is natural to turn to the insolubility of the oxide—a quality likely to oppose some difficulty in the way of establishing complete contact between the boric acid and the magnesia during a short exposure. Direct tests of this point showed distinctly that mixtures of boric acid in water and

magnesia, when submitted at once to distillation, yielded boric acid to the distillate ; but that, if the mixtures were permitted to stand some hours before distilling, the oxide passed to the semi-gelatinous condition of the hydrate, and retained the boric acid so firmly that turmeric failed to show the presence of the latter in the distillate. It is plain, therefore, that with sufficient preliminary exposure magnesia might be relied upon to retain boric acid ; but inasmuch as long and perhaps somewhat indefinite periods of waiting are objectionable in any analytical process, it was thought best to try the effect of substituting lime for magnesia. Experiments (9) to (12), conducted like the previous ones, except-ing only the use of carefully prepared and ignited calcium oxide instead of magnesium oxide, were made with this end in view.

	B_2O_3 taken.	CaO taken.	$CaO + B_2O_3$ found.	B_2O found.	Error.
	Gram.	Gram.	Gram.	Gram.	Gram.
(9)	0.1810	0.9737	1.1560	0.1823	0.0013 +
(10)	0.1819	0.9750	1.1583	0.1833	0.0014 +
(11)	0.1808	0.9922	1.1810	0.1818	0.0010 +
(12)	0.1833	0.9715	1.1560	0.1845	0.0012 +

These figures indicate sufficiently that there is no loss of boric acid by volatilisation when its aqueous solution is evaporated in contact with calcium hydrate ; but, inasmuch as the comparative solubility of the latter is the quality which makes it effective where magnesia is not, it seemed desirable to test the action of calcium hydrate in alcoholic solutions, in which it is very insoluble. The experiment showed that when the solution of boric acid in methyl or ethyl alcohol is put upon lime and distilled at once, loss is apt to take place, and sometimes to a very considerable amount, but that a short period of digestion, with occasional stirring—from five to fifteen minutes—is sufficient to obviate danger of volatilisation of boric acid.

It appears, therefore, that, free boric acid being easily volatilised by means of methyl alcohol and fixed completely by calcic hydrate, the separation of the acid from almost everything with which it occurs ordinarily, and its estimation subsequently, depend only upon the practicability of distilling it from its compounds in such company that it may be retained by lime, and its amount determined by the increase in the weight of the latter. Unlike magnesium chloride, calcium chloride does not yield its chlorine readily under

the action of heat and moisture naturally retained; so that hydro-
chloric acid must not be present with boric acid, which is to be
estimated in the manner described. Calcium nitrate and calcium
acetate both yield the oxide without difficulty upon ignition, and
nitric and acetic acids are suitable agents, therefore, for the libera-
tion of boric acid previous to distillation.

The actual distillation presented at first some difficulty—for the
repeated, thorough and rapid evaporation of a liquid charged
with soluble or insoluble solid matter is apt to involve some
mechanical transfer to the distillate of material which should re-
main in the residue—but the device of the following description
solves the problem successfully.
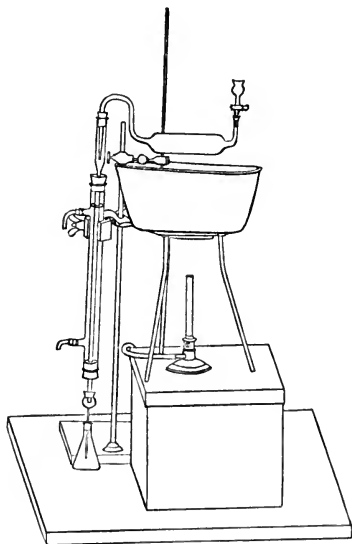
The apparatus, which is shown in the accompanying cut, con-
sists essentially of a retort, condenser, and bath for heating. For
the last I have used a paraffine bath, as being on the whole the
most convenient. The condenser is set vertically, to facilitate

changing the level of the retort within the bath, and to secure at the same time continual and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying-tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle, at the other to a goose-neck, as shown. To the former end is fitted, by a rubber stopper or section of tubing, a glass funnel-tube provided with a stopcock; the end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus, but it is convenient to attach to receive the distillate a small Erlenmeyer flask, which moves with the condenser and is joined to it, in the manner indicated in the figure, by means of a thistle-tube and a rubber stopper grooved to permit the free passage of air. In carrying out a distillation, the liquid to be distilled is introduced into the retort either by the funnel-tube or previous to its insertion, the glass cock is closed, the water started through the condenser, and the retort lowered into the hot paraffine, care being taken to begin the operation with the retort not more than half full and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked, it may sometimes happen that the sudden and violent expulsion of air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty, and requires little care.

The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a 200 cc. pipette makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 cc. of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it; 0.7 cc. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid which is to be distilled boils—something between 130° C. and 140° C. does very well for water, and is not too high for methyl alcohol—and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet without actual boiling.

With such an apparatus the following experiments were made : The boric acid was weighed, as before, in solution, and, to bring the condition of the experiment to that of an actual analysis, 1 gram of pure sodium hydrate was added in solution, nitric acid or acetic acid to acidity and a little more, and the whole was introduced into the retort and distilled to dryness.

In those experiments in which nitric acid was employed, the methyl alcohol was introduced upon the residue thus dried in six successive portions of 10 cc. each, and distilled to dryness ; but in order to break up the residue of sodium nitrate, which by its insolubility might effect to some extent the protection of the boric acid from the action of the alcohol, 2 cc. of water were introduced and evaporated between the second and third, and again between the fourth and fifth, distillations.

When acetic acid was made use of to free the boric acid, the six distillations with methyl alcohol were made as before ; but sodium acetate being soluble in methyl alcohol, the intermediate treatments with water were unnecessary. With the fourth portion of methyl alcohol a few drops of acetic acid were added to preserve the acidity of the residue, which, as has been pointed out, tends to become alkaline under the treatment.

The residues of both processes of treatment were found to be free from boric acid by the exceedingly delicate test with turmeric, care being taken in the series of experiments in which nitric acid was used to oxidise nitrates by means of bromine (expelling the latter before making the test), and in the acetic acid series to acidify with hydrochloric acid sufficiently to counteract the tendency of the acetate by itself to brown the turmeric on evaporatien.

The lime to retain the boric acid in the distillate was ignited in the crucible in which the evaporation of the distillate was to be made subsequently, and then transferred to the receiving flask attached to the condenser, so that the boric acid might be fixed during the distillation. To prevent the caking of the lime by the action of the alcohol, it was slaked with a little water before the distillation was begun.

In Experiments (13) to (16) nitric acid was employed, and in (17) to (20) acetic acid was used, with the precaution noted, to liberate the boric acid.

	B_2O_3 taken.	CaO taken.	B_2O_3+CaO found.	B_2O_3 found.	Error.
	Gram.	Gram.	Grams.	Gram.	Gram.
(13)	0.1738	0.9647	1.1392	0.1745	0.0007 +
(14)	0.1806	0.9639	1.1456	0.1817	0.0011 +
(15)	0.1779	0.9665	1.1450	0.1785	0.0006 +
(16)	0.1824	0.9739	1.1587	0.1848	0.0024 +
(17)	0.1806	1.4559	1.6371	0.1812	0.0006 +
(18)	0.1812	0.9720	1.1543	0.1823	0.0011 +
(19)	0.1788	0.9986	1.1781	0.1795	0.0007 +
(20)	0.1813	0.9527	1.1358	0.1831	0.0018 +

In Experiments (13) to (16) the mean error amounts to 0.0012 + gram; in Experiments (17) to (20) the mean error is a little more than 0.0010 + gram. Throughout the entire series of experiments the tendency to yield figures slightly larger than the truth is manifest, but the error is quite within legitimate limits. The greatest care was taken to secure similarity of conditions under which the crucible and lime were weighed before and after the evaporation and absorption of boric acid, and the weight after ignition was taken in every case after cooling over sulphuric acid during a definite period of ten minutes, in order to eliminate as far as possible the effect of atmospheric condensation upon the large surface of platinum. Ignitions were always finished over the blast-lamp, and constancy of weights secured.

The results of both modes of treatment are on the whole satisfactory, and equally so.

In the presence of chlorides, it is of course impossible to employ nitric acid to free the boric acid. Oxalic, citric, and tartaric acids also liberate hydrochloric acid to a considerable extent from alkaline chlorides. It was found, however, that when acetic acid was distilled over sodium and potassium chlorides, only traces of hydrochloric acid passed into the distillate, and Experiments (21) to (23) were made to determine whether these amounts are sufficient to vitiate the separation of boric acid from alkaline chlorides by distillation in presence of free acetic acid. The details of treatment were identical with those of Experiments (17) to (20), excepting only the addition of 0.5 gram of sodium chloride to each portion before distillation.

	B_2O_3 taken.	CaO taken.	B_2O_3+CaO found.	B_2O_3 found.	Error.
	Gram.	Gram.	Gram.	Gram.	Gram.
(21)	0.1834	0.9842	1.1675	0.1833	0.0001 −
(22)	0.1831	0.9755	1.1593	0.1838	0.0007 +
(23)	0.1761	0.9740	1.1523	0.1783	0.0022 +

The mean error of these results is about 0.0009+ gram, and it is plain that the presence of sodium chloride does not materially change the conditions of the experiment. There seems, therefore, to be no reason why boric acid may not be separated by distillation from alkaline chlorides in presence of free acetic acid ; but it was found that the presence of any considerable amount of potassium acetate is disadvantageous. Sodium acetate to a reasonable amount does not interfere with the favorable progress of the separation ; but potassium acetate appears to require a much higher temperature for the expulsion of its water, and longer distillation.

When, therefore, chlorides are present in the salts from which boric acid is to be removed by distillation, the choice is open between two methods : the distillation may be made directly with an excess of acetic acid ; or the hydrochloric acid may be first removed by means of silver nitrate, and the distillation of the filtrate proceeded with at once, or after precipitation of the excess of silver salt by means of sodium hydrate or carbonate, care being taken to acidify again sufficiently with nitric acid after the removal of the silver. Of these two modes of proceeding, I incline to the treatment with nitric acid and the removal of the chlorine by precipitation ; and this method has been used with success by others as well as myself, for some months, in the analysis of waters carrying boric acid, and natural borates.

The process in either modification is fairly accurate and easily executed, and admits of very wide application. Insoluble compounds in which the boric acid is to be determined may be dissolved in nitric acid at once, or, if necessary, first fused with sodium carbonate ; and, fortunately, nearly everything which is volatile in the subsequent treatment, and capable of forming with lime compounds not easily decomposable by heat, may be removed by known processes. The combination of fluorine, silica, and boric acid is perhaps most difficult to treat ; but the precipitation and removal of the first as calcium fluoride from the aqueous solution of a fusion in alkaline carbonate may, it is believed, be effected with care, and the mode of procedure from that point is simple.

The number of distillations necessary depends, of course, upon the amount of boric acid treated. To remove 0.2 gram of boric anhydride completely to the distillate, six charges of methyl alcohol, of 10 cc. each, proved, as we have seen, to be ample.

The apparatus by the aid of which the distillation processes

which have been described were carried out has found useful application in a number of other processes. In the determination of free and albuminoid ammonia in waters which can be boiled quietly with difficulty, in the methods of estimating hydrofluoric acid which involve the expulsion of silicon fluoride from a mixture of the fluoride with sulphuric acid and silica, in the separation of iodine from bromides and chlorides by distilling with ferric sulphate and sulphuric acid, and of bromine from chlorides by means of per- manganic acid, it has proved of value, and will doubtless be found convenient in many analytical processes in which quantitative sepa- rations by the distillation of liquids liable to spatter or boil explosively are involved.

A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES.

With Some Reference to a Similar Separation of the Same from Magnesium and Calcium.

By F. A. Gooch.

For the quantitative separation of lithium from sodium and potas- sium, Mayer's method,[1] which is based upon the precipitation of lithium as the tribasic phosphate, and Rammelsberg's[2] mode of parting the chlorides by means of a mixture of anhydrous alcohol and ether in equal parts, have been available.

The method of Mayer grew out of the older process of Ber- zelius,[3] which consisted essentially in treating the solution of the alkaline salts with phosphoric acid and sodium carbonate in excess, evaporating to dryness, and extracting with cold water. The result of a single analysis of the product thus obtained was the testimony upon which Berzelius rested the belief and statement that the salt was a double phosphate of lithium and sodium, which left upon ignition sodium and lithium pyrophosphates in equal molecules; and on this Berzelius based his process for the estima- tion of lithium. Rammelsberg,[4] however, showed later that it was

[1] Ann. d. Chem. u. Pharm. **98**, 193.   [2] Pogg. Ann. **66**, 79.
[3] *Ibid.* **4**, 245.   [4] *Loc. cit.*

a tribasic phosphate which was actually obtained, and from his experiments arrived at the conclusion that the proportions of soda and lithia were variable within wide limits, the amounts of the former varying in the special cases investigated from 7.84 per cent. to 28.38 per cent. ; and the same thing in substance was reiterated subsequently [1] in an account of a repetition of the work suggested by the criticism of Mayer. Mayer,[2] however, was unable to prepare under any conditions the double phosphate of Rammelsberg, and obtained invariably, when the preparation had been washed with sufficient care, trilithium phosphate free from sodium ; but the point was made that the phosphate is apt to be contaminated with lithium carbonate when sodium carbonate is employed to bring about alkalinity. Mayer therefore modifies the method of Berzelius by substituting sodium hydrate for the carbonate ; and, proceeding, evaporates to dryness, treats the dry mass with as much water as is needed to dissolve the soluble salts with the aid of heat, adds a drop or two of sodium hydrate if necessary to restore alkalinity, and then ammonia in volume equal to that of the water already added, sets aside at a gentle heat, filters only after twelve hours, and washes with a mixture of ammonia and water in equal parts. From the filtrate and first washings a small amount of the lithium phosphate is to be recovered by evaporation and the repetition of the former treatment. According to Mayer, the precipitation of the phosphate may be effected with equal completeness by boiling the solution, prepared as before, instead of evaporating it ; but the objection to this mode of proceeding is the tendency of the liquid carrying the precipitate to bump explosively. Careful washing, somewhat prolonged, is essential to secure the complete removal of salts of sodium and potassium, and it is remarked that the purity of the precipitate is shown by its failure to cake when strongly ignited.

This is the mode of proceeding by which Mayer separates lithium from sodium and potassium, isolating it as presumably pure trilithium phosphate and weighing it as the anhydrous salt. In dealing with mixtures of the chlorides in which the proportion of the lithium salt is relatively small, the removal of the greater part of sodium and potassium chlorides by a preliminary treatment with absolute alcohol is recommended. The following table comprises the results of Mayer's test analyses of lithium carbonate in the first

[1] Pogg. Ann. **102**, 443.   [2] *Loc. cit.*

seven, of lithium sulphate in the last two, recalculated with the use of the number 7—the figure now generally accepted as the atomic weight of lithium:

Li_3PO_4 equivalent to salt taken. Grams.	Li_3PO_4 found. Grams.	Error. Grams.
1.3586	1.3719	0.0133+
1.5172	1.5088	0.0084—
0.7519	6.7580	0.0061+
0.9561	0.9510	0.0051—
1.2651	1.2646	0.0005—
1.2197	1.2230	0.0033+
0.8991	0.9018	0.0027+
1.1325	1.1236	0.0089—
0.9715	0.9665	0.0050—

Fresenius[1] found, on examining the method, that several repetitions of the treatment by evaporation and extraction were required to complete the recovery of all lithium phosphate, and advised that the operation be continued until residual lithium phosphate fails to appear. The results of Fresenius's experiments with lithium carbonate, recalculated with the use of the number 7 as the atomic weight of lithium, are given in the table appended:

Li_3PO_4 equivalent to salt taken. Gram.		Li_3PO_4 found. Dried at 100° C. Gram.	Li_3PO_4 found. Ignited. Gram.	Error. Gram.
0.7443	after two treatments	0.7243	...	0.0200—
	" three "	0.7385	...	0.0058—
	" four "	0.7433	...	0.0010—
0.9820		0.9861	...	0.0041+
		...	0.9826	0.0006+
1.6341		1.6342	...	0.0001+
		...	1.6305	0.0036—

Thus it will be seen that in the nine experiments of Mayer the error ranges from 0.0133+ gram to 0.0089— gram, and that of the determinations of Fresenius from 0.0001+ gram to 0.0041+ gram for the dried precipitate, and from 0.0006+ gram to 0.0036— gram for the ignited precipitate.

If the tendency of lithium carbonate to fall in company with the phosphate were not to assert itself during the evaporations of solutions of salts of lithium in presence of sodium hydrate and in con-

[1] Zeit für anal. Chem. 1, 42.

tact with ordinary atmospheric air, it would surely be strange, and
this point may be fairly set down as one of the weak ones of the
method; but the gravest source of error, and that indicated most
unmistakably throughout the whole history of the process—which
has been recounted at some length for the purpose of emphasising
this very matter—is the impossibility of preparing the lithium
phosphate in anything like a condition of freedom from other alka-
line phosphates without a careful and prolonged washing, which
is sure to result in loss of the lithium salt by solution. When it is
remembered that according to Mayer's determinations trilithium
phosphate requires for solution only 2539 parts of water, or 3920
parts of a mixture of ammonia and water in equal portions, it is
plain that the success of the method depends upon the ability of
the analyst to wash to a condition of purity, and without loss of
that which it is the purpose of the process to save, a precipitate
peculiarly prone to retain foreign matter and soluble in the wash-
ing mixture in the proportion of ten milligrams to every 40 cc. of
the latter. Of course washings will never be entirely saturated,
nor will the precipitate be as soluble at the beginning of the opera-
tion as at the end, when the precipitant no longer exerts an action
which tends to lessen solubility; but, in view of the difficulties which
present themselves, it is sufficiently obvious that exact results
obtained by Mayer's process owe their apparent accuracy to a for-
tuitous balance of errors. The difference of 0.0222 gram between
the extremes of Mayer's experimental results should not be sur-
prising; and, at the best, the process is tedious and not entirely
trustworthy—facts of which its author was not unmindful.

In Rammelsberg's method of separating lithium chloride from
the chlorides of sodium and potassium the sources of error are, in
brief, the solubility of sodium chloride and potassium chloride in
the ether-alcohol mixture, the influence which the presence of
small amounts of water exerts upon the solubility of these same
salts, the difficulty of bringing the chlorides to the anhydrous
condition without decomposing the lithium chloride to a greater
or less extent, and the mechanical difficulties of transferring the
fused or crusted chlorides to a suitable receptacle for digestion and
agitation in the solvent, and of extracting perfectly the soluble con-
stituents of closely compacted matter. Of the last two items
nothing need be said in explanation beyond simply noting them.
The third is particularly important, inasmuch as the tendency of
lithium chloride, first noted, I believe, by Mayer, to exchange

chlorine for oxygen when ignited in presence of water, results in
the formation of lithium hydrate, or, in contact with products of
combustion, lithium carbonate, both of which are insoluble in the
mixture of ether and alcohol, and remain with the sodium and
potassium chlorides. As to the effect of water in the mixture, an
experiment of Mayer, in which it was found that 100 cc. of a
mixture of alcohol of 96 per cent. and ether of 98 per cent. dis-
solved 0.1100 gram of sodium chloride, is instructive. In regard
to the solubility of the chlorides of sodium and potassium in the
mixture of anhydrous ether and alcohol, Rammelsberg's statement,
that from 0.9770 gram of pure, strongly heated sodium chloride
with an undetermined amount of lithium chloride the mixture
extracted 0.0130 gram, is unfortunately meaningless in the
absence of information concerning the amount of solvent em-
ployed. J. Lawrence Smith[1] found, in making an examination of
this matter, that 10 cc. of the anhydrous ether-alcohol mixture
extracted from 0.5 gram of sodium chloride 0.0005 gram, and
from 0.5 gram of potassium chloride 0.0003 gram. Smith's mode
of applying the method is better than the original; for, by taking
care not to heat the mixed salts above 100° C., the danger of
decomposing the lithium chloride is diminished, and by treating
the dried salts with the ether-alcohol mixture in the capsule in
which it is heated and weighed (protecting it by a small inverted
bell-glass) the disadvantage of the transfer is avoided, but the
danger is incurred that the mixed salts may not be thoroughly
dried by heat so gentle. With this modification Smith obtained
results which are rearranged in the following statement, and which
do not throw a very favorable light upon the method:[2]

NaCl taken. Gram.	KCl taken. Gram.	LiCl taken. Gram.	Weight dissolved. Gram.	Error. Gram.
0.2000	0.2000	0.0080	0.0101	0.0021+
0.2000	0.2000	0.0884	0.0862	0.0022—
0.2000	0.2000	0.8195	0.8341	0.0146+

[1] Am. Jour. Sci. [2] **16**, 56.

[2] Dr. Smith's language in the description of these experiments is somewhat ambiguous, but
it is believed that these figures represent the meaning intended. After the presentation of the
data of the first experiment given here with the correction of an obvious typographical error,
it is said of the second and third experiments that "a similar mixture containing 18.20 per
cent. of chloride of lithium furnished a residue of 17.65 per cent.," and "a similar mixture
containing 67.20 per cent. of chloride of lithium gave a residue of 68.40." I have taken this to
mean that in all three experiments 0.2 gram of sodium chloride and 0.2 gram of potassium
chloride were employed with the different proportions of lithium chloride indicated for each
experiment. At all events, if this is not the meaning of the language made use of, it is difficult
to see a definite value in the experiments.

It is obvious, therefore, that neither the method of Rammels-berg nor that of Mayer may justly claim to be what a good process should be—accurate and rapid—and in the dilemma many chemists have been inclined to accept, with Bunsen,[1] the inherent disadvantage of an indirect process, and in a mixture of sodium and lithium chlorides calculate the percentage of each from the known weight of the mixture and its contents in chlorine, and in a mixture of the three chlorides calculate the percentage of each from the known weight of the mixture and the determined contents in chlorine and potassium. Here again, however, as in Rammelsberg's process, the difficulty of bringing the chlorides to a definite condition for weighing without decomposing the lithium chloride is an obstacle ; and in case potassium is to be separated from large amounts of lithium by precipitation as potassio-platinic chloride, the concurrent precipitation of a similar salt of lithium, to which Jenzsch[2] has directed attention, may be the occasion of inexactness. So, the intrinsic unsatisfactoriness of indirect methods quite aside, it appears that in following Bunsen we have by no means all that is to be desired in an analytical method.

In looking about for better means for the separation of lithium from sodium and potassium, certain preliminary experiments on the behavior of the chlorides of these elements toward amyl alcohol gave very encouraging indications, and subsequent quantitative tests have borne out the hope that a successful method of separation might be based upon these relations.

In amyl alcohol the chlorides of sodium and potassium are highly insoluble, lithium chloride dissolves freely, and the attraction of amyl alcohol for water is so slight and its boiling-point so far above 100° C. that the latter may be expelled without difficulty by the aid of gentle heating.

When amyl alcohol is poured into a solution of lithium chloride in water, the liquid forms two layers, the aqueous solution of the salts at the bottom and the amyl alcohol now carrying a little water above. With the application of heat the water evaporates slowly, then boils, and, passing through the alcohol, escapes, until toward the end of the operation the residual lithium chloride collects in a viscous globule, and finally dissolves with the exception of a slight incrustation. If now the alcohol is cooled and a drop of strong hydrochloric acid added and brought in contact with the deposit,

[1] Ann. d. Chem. u. Pharm. **122**, 348.   [2] Pogg. Ann. **104**, 102.

and the boiling repeated, the solution is complete. This deposit I take to be lithium hydrate, resulting from the decomposition of the chloride by the protracted action of water at a temperature near its boiling-point. The small amount of water which is added in and with the hydrochloric acid seems to exert no unfavorable influence, but rather to be beneficial in hastening the solution of the residue by securing immediate and sufficient contact.

In hot amyl alcohol lithium chloride appears to be a little more soluble than in the same reagent at ordinary temperatures, but the solubility under the latter condition only was determined. By boiling the solution until turbidity began to show, cooling, filtering, and then evaporating a known volume of the concentrated solution to dryness and weighing the residue after converting it to the sulphate, it was found that one part of lithium chloride was held dissolved in the cold in about fifteen parts of amyl alcohol, 10 cm.³ of the solution containing in the mean 0.66 gram of the chloride.

When aqueous solutions of sodium chloride or potassium chloride are treated with amyl alcohol and boiled, the water disappears, as before, leaving first a globule of the concentrated solution and finally the crystalline salts. On continuing the boiling until a thermometer dipped in the liquid indicates the temperature at which the alcohol boils by itself, a slight additional precipitation, doubtless due to the expulsion of the water retained by the alcohol up to this point, takes place upon the walls of the containing vessel. The results of quantitative tests of the solubility of sodium and potassium chlorides are given in the following tables. The strength of the solutions of sodium chloride and potassium chloride was determined by evaporating weighed portions in a platinum crucible and drying at a temperature considerably below the melting point of the salt, and weighing. The solution of lithium chloride was standardised by treating a weighed portion with sulphuric acid in excess, evaporating, igniting at red heat, and weighing. The standards were fixed by Experiments (1) to (9).

	Weight of Solution of NaCl taken. Grams.	Weight of NaCl found. Gram.	Weight of NaCl in 10 grams of Solution. Gram.	Mean. Gram.
(1)	10.7110	0.1072	0.1001	
(2)	10.9419	0.1097	0.1003	0.1002
(3)	10.9325	0.1097	0.1003	

Weight of Solution of KCl taken. Grams.	Weight of KCl found. Gram.	Weight of KCl in 10 grams of Solution. Gram.	Mean. Gram.
(4) 9.3045	0.1744	0.1874 ⎫	
(5) 10.7225	0.2006	0.1871 ⎬	0.1872
(6) 11.1974	0.2096	0.1872 ⎭	

Weight of Solution of LiCl taken. Grams.	Weight of Li$_2$SO$_4$ found. Gram.	Weight of LiCl in 10 grams of Solution. Gram.	Mean. Gram.
(7) 10.9280	0.1635	0.1156 ⎫	
(8) 11.1480	0.1665	0.1153 ⎬	0.1154
(9) 10.8790	0.1626	0.1154 ⎭	

To determine the solubility of sodium chloride and potassium chloride in amyl alcohol, portions of the test solutions were weighed out, evaporated to a convenient bulk in platinum crucibles of 100 cc. capacity, amyl alcohol was added, the water expelled by boiling, and the heating continued for some minutes after the thermometer in the liquid indicated 132° C., the boiling-point of the alcohol employed. The liquid was then decanted with care and the residue dried at a temperature below its melting-point and weighed. When the chlorides are precipitated in the manner described, the deposit generally adheres so closely, and such particles as do remain loose settle so well, that the supernatant liquid may be decanted to the end without appreciable transportation of the insoluble residue. For the sake of perfect security, however, in this part of the manipulation the decanted liquid was filtered under gentle pressure upon asbestos, with the aid of the device which I have previously described for such purposes,[1] and, after gentle heating, the increase in weight of the felt and the containing perforated crucible added to the weight of the residual salt. In no case did this increase exceed a few tenths of a milligram, and often could not be detected.

As a source of heat, a bath in which the sand of the sand-bath is replaced by smooth asbestos board is a convenience, or a piece of asbestos board simply, about 30 cc. square, supported by a broad tripod and heated under the middle by a Bunsen burner, answers equally well to secure every gradation of heat without danger of igniting the evaporated alcohol.

As a control upon the results obtained by weighing the residue as described, the filtrate was evaporated in a large platinum crucible, and the residue thus left gently heated and weighed. Though

the evaporation be conducted with extreme care, the residue is almost sure to show some blackening, due to the carbonisation of matter carried by the alcohol, which will not disappear entirely without the application of a degree of heat which the salts cannot bear without danger of volatilisation. The weight of the residue from the amyl alcohol itself is small — one portion of 50 cc. yielding 0.0003 gram and its mate 0.0007 gram—so that the data obtained by the evaporation of the filtered alcohol of the experiments, if not quite so trustworthy as the former testimony, may nevertheless serve the purpose of a very close control. Both sets of data are given in the following table:

	Weight of NaCl taken.	Total Weight of NaCl found.	Weight found in Residue.	Weight found in Solution.	Volume of Residual Amyl Alcohol.
	Gram.	Gram.	Gram.	Gram.	Cc.
(10)	0.1062	0.1067	0.1043	0.0024	52
(11)	0.1043	0.1047	0.1024	0.0023	46
(12)	0.1024	0.1030	0.1003	0.0027	51
(13)	0.1003	0.1008	0.0983	0.0025	45

Reducing these figures to a common level to show the action of the same amount of amyl alcohol in every case, we have:

	Loss of NaCl to 100 cc. of Amyl Alcohol.	Mean.	Weight of NaCl found in Solution in 100 cc. of Amyl Alcohol.	Mean.
	Gram.	Gram.	Gram.	Gram.
(10)	0.0037		0.0046	
(11)	0.0041	0.0041	0.0050	0.0051
(12)	0.0041		0.0053	
(13)	0.0044		0.0055	

	Weight of KCl taken.	Total Weight of KCl found.	Weight found in Residue.	Weight found in Solution.	Volume of Residual Amyl Alcohol.
	Gram.	Gram.	Gram.	Gram.	Cc.
(14)	0.2091	0.2093	0.2074	0.0019	35
(15)	0.2074	0.2078	0.2059	0.0019	36
(16)	0.2059	0.2059	0.2040	0.0019	32
(17)	0.2040	0.2041	0.2015	0.0026	45

Derived from these figures we have:

	Loss of KCl to 100 cc. of Amyl Alcohol.	Mean.	Weight of KCl found in Solution in 100 cc. of Amyl Alcohol.	Mean.
	Gram.	Gram.	Gram.	Gram.
(14)	0.0049		0.0054	
(15)	0.0041	0.0051	0.0053	0.0056
(16)	0.0059		0.0059	
(17)	0.0056		0.0058	

From these figures it appears that the total weight of chloride found is always a little greater than that taken, the mean increase being 0.0005 gram for sodium chloride, and 0.0002 gram for potassium chloride. It appears also that the residue left by the evaporation of the decanted and filtered amyl alcohol is greater than the loss put upon the chloride by the treatment—in the case of sodium chloride 0.0005 gram, in the mean, for every 50 cc. of amyl alcohol, which is about the quantity employed in the experiments; for potassic chloride 0.0002 gram, in the mean, for 40 cc. of amyl alcohol, which is approximately the quantity used in that case. It will be seen, therefore, that there exists for both salts an exact coincidence between the mean total excess found and the difference between the figures which indicate the solubility of the salts for the two methods of determination; and, taking this fact in conjunction with the results of the evaporation of amyl alcohol in blank—the mean residue being 0.0004 gram for 40 cc., and 0.0005 gram for 50 cc.—it seems to be brought out pretty clearly that the former set of figures represents more exactly the solubility of the salts, though the difference between the two series is not great. Resting, then, upon the former determinations, the solubility of sodium chloride may be taken as 0.0041 gram in every 100 cc. of anhydrous amyl alcohol, or one part in 30,000 parts by weight; and the solubility of potassium chloride, a little greater, is 0.0051 gram to 100 cc. of amyl alcohol, or one part in 24,000 by weight.

The conditions under which the salts are acted upon are such as should insure the complete saturation of the solvent, and in this connection it is interesting to note that for the quantities of material employed the discrepancy between comparable figures never exceeds 0.0005 gram.

In Experiments (10), (11) and (14), (15), the alcohol was decanted and filtered at once while hot; in (12), (13) and (16), (17), it was cooled to 30° C. before decanting; so it appears that the solubility of the salts is not influenced by changes of temperature within the range from 30° C. to 132° C.

Used simply to wash the precipitate, amyl alcohol cannot, of course, exert an effect at all comparable with that manifested in the experiments which have been described, but to know just what this action may be is important. Experiments (18) to (22) were undertaken, therefore, to elucidate this point.

Weighed amounts of the test solutions were evaporated nearly to saturation in small glass beakers, amyl alcohol added, and, as in the previous experiments, the whole heated until the salt had deposited and the residual alcohol had boiled quietly for some minutes at its ordinary boiling-point, the liquid decanted, filtered under gentle pressure by means of a weighed perforated crucible and felt of asbestos, the filtrate measured, the residue dislodged with the aid of a rubbing-rod, and transferred to the crucible and washed with anhydrous amyl alcohol, the washings being collected and measured. The crucible and contents were dried over a free flame turned low, so that the heat should not reach the melting point of the chlorides.

	Weight of NaCl taken.	Weight of NaCl found.	Weight of NaCl found, corrected for Solubility in Residual Amyl Alcohol.	Error of Corrected Weight of NaCl found.	Volume of Residual Amyl Alcohol.	Volume of Amyl Alcohol in Washings.
	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.
(18)	0.0947	0.0937	0.0947	0.0000	24	44
(19)	0.1080	0.1074	0.1082	0.0002+	19	53

	Weight of KCl taken.	Weight of KCl found.	Weight of KCl found, corrected for Solubility in Residual Amyl Alcohol.	Error of Corrected Weight of KCl found.	Volume of Residual Amyl Alcohol.	Volume of Amyl Alcohol in Washings.
	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.
(20)	0.1846	0.1837	0.1847	0.0001 +	20	60
(21)	0.1964	0.1946	0.1961	0.0003—	30	45
(22)	0.1857	0.1839	0.1854	0.0003—	30	60

These results show very plainly that the solvent effect of anhydrous amyl alcohol used for washing under the conditions described is trifling in the extreme, and may be neglected utterly, providing the amount of the washing is not altogether disproportionate to the needs of the case.

We pass next to the consideration of the separation of the chlorides of sodium and potassium from lithium chloride. Weighed portions of the test solutions were concentrated and treated with amyl alcohol in the manner described until the precipitated salt was entirely free from water and the supernatant alcoholic solution of the lithium chloride boiled constantly at a point not far from that of the amyl alcohol employed. Then the liquid was cooled, a drop or two of strong hydrochloric acid added in accordance with the evident suggestion of the preliminary experiments previously mentioned, and heat again applied until the boiling had con-

tinued, as before, for some minutes at one point. The filtration, washing, drying, and weighing of the residue were effected as in Experiments (18) to (22). In those of the experiments in which the lithium salt in solution was also determined, the end was accomplished by evaporating the filtrate and washings to dryness, treating the residue with sulphuric acid, and igniting and weighing as lithium sulphate. In the following table the weight of insoluble chloride actually found is given in one column, and this weight, corrected according to the data previously determined for the solubility of the chloride in the residual amyl alcohol, appears in the column adjoining. So, also, the weight is given of the lithium sulphate actually found, and an adjacent column contains the result of correcting this weight for the accompanying sodium or potassium sulphate, or both, upon the hypothesis that these salts are neutral sulphates after the ignition. In the case of quantities so minute, the error which is introduced by such an assumption cannot be considerable, and in relation to this point Dittmar[1] maintains that comparatively large amounts of acid sodium or potassium sulphate may be reduced to the neutral salt by ignition simply. The figures of the column showing the weights of lithium chloride found are derived by calculation from the weights of lithium sulphate actually found. The other headings of the table are sufficiently intelligible without further explanation.

	Weight of NaCl taken.	Weight of NaCl found.	Weight of NaCl found, corrected for Solubility in Amyl Alcohol.	Error in Weight of NaCl found.	Error in Corrected Weight of NaCl found.	Volume of Amyl Alcohol used. Resid-ual.	Total.
	Gram.	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.
(23)	0.1089	0.1092	0.1095	0.0003+	0.0006+	7	70
(24)	0.1084	0.1085	0.1090	0.0001+	0.0006+	12	80
(25)	0.1074	0.1067	0.1074	0.0007—	0.0000	18	90

	Weight of LiCl taken.	Weight of Li_2SO_4 found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in Corrected Weight of LiCl found.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
(23)	0.1298	0.1682	0.1299	0.1296	0.0001+	0.0002—
(24)	0.1227	0.1592	0.1230	0.1225	0.0003+	0.0002—
(25)	0.0116	...	...	...	...	...

[1] Report on Researches into the Composition of Ocean Water, collected by H. M. S. Challenger during the Years 1873-1876, p. 18.

	Weight of KCl taken.	Weight of KCl found.	Weight of KCl found, corrected for Solubility in Amyl Alcohol.	Error in Weight of KCl found.	Error in Corrected Weight of KCl found.	Volume of Amyl Alcohol used. Residual. Total.
	Gram.	Gram.	Gram.	Gram.	Gram.	Cc. Cc.
(26)	0.2051	0.2036	0.2053	0.0015—	0.0002+	34 100
(27)	0.2022	0.2013	0.2032	0.0009—	0.0010+	37 100
(28)	0.2109	0.2096	0.2104	0.0013—	0.0005—	16 100
(29)	0.0984	0.0970	0.0980	0.0014—	0.0004—	20 90

	Weight of LiCl taken.	Weight of Li$_2$SO$_4$ found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in Corrected Weight of LiCl found.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
(26)	0.1256	0.1638	0.1265	0.1248	0.0009+	0.0008—
(27)	0.1287	0.1677	0.1296	0.1277	0.0009+	0.0010—
(28)	0.0113	...	...	...	...	...
(29)	0.0113	...	...	...	...	...

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl+KCl found.	Corrected Weight of NaCl+KCl found.	Volume of Amyl used. Residual. Total.
	Gram.	Gram.	Gram.	Gram.	Cc. Cc.
(30)	0.1053	0.1031	0.2064	0.2084	22 100
(31)	0.1051	0.0945	0.1988	0.2003	16 80

	Weight of LiCl taken.	Error in Weight of NaCl + KCl found.	Error in Corrected Weight of NaCl + KCl found.
	Gram.	Gram.	Gram.
(30)	0.0113	0.0020—	0.0000
(31)	0.0113	0.0008—	0.0007+

It will be noticed that in Experiments (23), (24), (26) and (27), the corrected error in the weight of the insoluble chloride has a positive value ranging from 0.0002+ gram to 0.0010+ gram with a mean of 0.0006+ gram; and that in Experiments (25), (28), (29), (30) and (31), the mean error is negative, amounting to less than 0.0001— gram, with a range from 0.0005— gram to 0.0007+ gram.

The point of difference between these two series of experiments is the amount of lithium chloride introduced, only a tenth of that used in the former being employed in the latter. It is plain that, when we are dealing with the larger amount, a larger portion tends to remain behind with the insoluble chloride; and here again we meet, though to a degree comparatively harmless, the inclination of lithium chloride to yield chlorine and pass to the form of lithium hydrate. When the lithium chloride is present in small amount, as in the latter group of experiments, there can be little left undis-

solved; and the spectroscope confirms the evidence of the figures of analysis as to the perfectness of the separation, by showing in such cases either no lithium at all or merely fugitive traces. If a single precipitation is sufficient to effect a satisfactory separation of the insoluble chlorides from small amounts of lithium chloride, it is natural to suppose that a repetition of the precipitation would be beneficial in treating larger quantities of lithium chloride. Experiments (32) to (37) illustrate the effect of a double precipitation. The chlorides were brought to filtration as before, the liquid was decanted as completely as possible, the precipitate washed slightly by decantation and redissolved in a little water, and the round of boiling, filtering, drying, and weighing carried to the end as before, care being taken to repeat the treatment with a drop of hydrochloric acid during the process of boiling. The two portions of residual amyl alcohol were measured apart, as well as the washings.

	Weight of NaCl taken.	Weight of NaCl found.	Corrected Weight of NaCl found.	Error in Weight of NaCl found.	Error in Corrected Weight of NaCl found.	Volume of Amyl Alcohol used. Residual. Total.		
						I. Cc.	II. Cc.	Cc.
	Gram.	Gram.	Gram.	Gram.	Gram.			
(32)	0.1166	0.1163	0.1169	0.0003—	0.0003+	8	8	150
(33)	0.1139	0.1127	0.1132	0.0012—	0.0007—	5	7	150

	Weight of LiCl taken.	Weight of Li$_2$SO$_4$ found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in Corrected Weight of LiCl found.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
(32)	0.1287	0.1662	0.1284	0.1280	0.0003—	0.0007—
(33)	0.1347	0.1759	0.1359	0.1353	0.0012+	0.0006+

	Weight of KCl taken.	Weight of KCl found.	Corrected Weight of KCl found.	Error in Weight of KCl found.	Error in Corrected Weight of KCl found.	Volume of Amyl Alcohol used. Residual. Total.		
						I. Cc.	II. Cc.	Cc.
	Gram.	Gram.	Gram.	Gram.	Gram.			
(34)	0.1155	0.1142	0.1152	0.0013—	0.0003—	10	10	100
(35)	0.1034	0.1017	0.1028	0.0017—	0.0007—	10	12	200
(36)	0.1914	0.1905	0.1912	0.0009—	0.0002—	3	11	90
(37)	0.1953	0.1939	0.1950	0.0014—	0.0003—	4	18	110

	Weight of LiCl taken.	Weight of Li$_2$SO$_4$ found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in Corrected Weight of LiCl found.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
(34)	0.1125	0.1475	0.1139	0.1128	0.0014+	0.0003+
(35)	0.1251	0.1649	0.1274	0.1162	0.0023+	0.0011+
(36)	0.1263	...	...	...	...	...
(37)	0.1282	...	...	...	...	...

Thus it appears that, in the separation of the insoluble chlorides from the larger amounts of lithium chloride, the residue of two precipitations is substantially free from lithium.

For the sake of bringing the data in hand more directly into comparison, the corrected errors of the preceding determinations are tabulated again in the following statement:

No. Exp.	Chloride.	Corrected error of insoluble chloride			Error in corrected Weight of LiCl. Gram.	Approximate Mean Error of LiCl. Gram.
		once from about 0.13 Gram of LiCl. Gram.	*once* from about 0.013 Gram of LiCl. Gram.	*twice* from about 0.13 Gram of LiCl. Gram.		
(23)	NaCl	0.0006+	...	...	0.0002—	
(24)	"	0.0006+	...	...	0.0002—	
(26)	KCl	0.0002+	...	...	0.0008—	0.0005—
(27)	"	0.0010+	...	...	0.0010—	
(25)	NaCl	...	0.0000	...	...	
(28)	KCl	...	0.0005—	...	...	
(29)	"	...	0.0004—	...	...	
(30)	NaCl+KCl	...	0.0000	...	...	
(31)	" "	...	0.0007+	...	...	
(32)	NaCl	...	...	0.0003+	0.0007—	
(33)	"	...	...	0.0007—	0.0006+	
(34)	KCl	...	...	0.0003—	0.0003+	0.0003+
(35)	"	...	...	0.0007—	0.0011+	
(36)	"	...	...	0.0002—	...	
(37)	"	...	...	0.0003—	...	

Approx. mean, 0.0006+ 0.00004— 0.0003—

Few processes in analytical chemistry are capable of yielding results more exact than these. The separation of from 0.1 gram to 0.2 gram of sodium or potassium chloride from a tenth of its own weight of lithium chloride is practically perfect in one operation, and from its own weight of lithium chloride the parting may be effected satisfactorily by two precipitations.

The points to be observed in executing the method may be recapitulated as follows:

To the concentrated solution of the chlorides, amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until, the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a tem-

perature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is small it will now be found in solution, and the chlorides of sodium and potassium will be in the residue, excepting the traces, for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds ten or twenty milligrams, it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol previously dehydrated by boiling is to be used, and the filtrates are to be measured apart from the washings. In filtering it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0.00041 gram for every 10 cc. of amyl alcohol in the filtrate, exclusive of washings, if the insoluble salt is entirely sodium chloride, 0.00051 gram for every 10 cc. if potassium chloride constitutes the residue, and if both sodium and potassium chloride are present, 0.00092 gram ; but, as in the experiments described, the entire correction may in any case be kept within narrow limits if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the latter driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of 0.00050 gram is to be made if sodium chloride constitutes the precipitate, 0.00059 gram if potassium chloride alone is present in the residue, and 0.00109 gram if both of these chlorides are present, for every 10 cc. of filtrate exclusive of washings.

Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature—the development of the

fumes of amyl alcohol—is one which is insignificant when good ventilation is available.

The process has been used for some months frequently and successfully, by others as well as myself, for the estimation of lithium in waters and minerals.

In this connection it seems best to include the record of certain experiments looking to the separation of the chlorides of sodium and potassium from the chlorides of magnesium and calcium. The behavior of magnesium chloride toward amyl alcohol is of interest, both with reference to the problem of separating sodium and potassium from lithium and magnesium when the latter are associated, and as concerns the parting of the alkalies from magnesium alone—a matter which is by no means perfectly simple—and Experiments (38) to (41) touch upon this topic.

The chlorides of sodium and potassium were weighed, as before, in solution; the magnesium chloride was obtained by dissolving in hydrochloric acid the oxide specially prepared and weighed as such. The process of treatment was identical with that just described for the separation of the chlorides of potassium and sodium from lithium chloride.

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl+KCl found.	Corrected Weight of NaCl+KCl found.	Volume of Amyl Alcohol used. Residual.		Total
					I.	II.	
	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Cc.
(38)	0.1030	0.1064	0.2079	0.2100	23	...	120
(39)	0.0967	0.1024	0.1976	0.2006	33	...	100
(40)	0.1030	0.1073	0.2071	0.2093	13	11	100
(41)	0.1053	0.1093	0.2114	0.2142	12	18	100

	Weight of MgO taken.	Error in Weight of NaCl+KCl found.	Error in Corrected Weight of NaCl+KCl found.
	Gram.	Gram.	Gram.
(38)	0.1000	0.0015—	0.0006+
(39)	0.1000	0.0015—	0.0015+
(40)	0.1000	0.0032—	0.0010—
(41)	0.1000	0.0032—	0.0004—

The residues of Experiments (38) and (39), in which the separation was made by a single precipitation, carried traces of magnesia; those of (40) and (41), in which two precipitations were introduced, were found to contain in the one case no magnesia, and in the other an unweighable trace. These results point out a method by

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which the chlorides of sodium and potassium may be obtained
free from magnesia, while the small amounts of the former which
pass into solution with the magnesium chloride are capable of
accurate estimation; and there seems to be no reason why the
separation of these alkaline chlorides from magnesium chloride
and lithium chloride occurring together should not be effected in
one operation, and the parting of the latter salts brought about by
the familiar method of precipitating the magnesia in the cold as
ammonium-magnesium phosphate.

Experiments (42) to (48), upon the separation of sodium and
potassium from calcium by the action of amyl alcohol on the
chlorides, yielded the figures of the following table. The mode
of treatment was identical with that of the experiments with mag-
nesia just described, excepting only the substitution of pure
calcium oxide, specially prepared, for magnesium oxide.

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl+KCl found.	Corrected Weight of NaCl+KCl found.	Volume of Amyl Alcohol used.		
					Residual.		Total.
					I.	II.	
	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Cc.
(42)	0.0859	0.1126	0.2177	0.2195	20	...	100
(43)	0.1018	0.1057	0.2217	0.2235	20	...	100
(44)	0.1096	0.0962	0.2112	0.2130	20	...	100
(45)	0.0985	0.1018	0.2113	0.2130	19	...	100
(46)	0.0914	0.1104	0.1968	0.2000	20	15	100
(47)	0.0997	0.1100	0.2080	0.2089	3	7	90

	Weight of CaO taken.	Error in Weight of NaCl+KCl found.	Error in Corrected Weight of NaCl+KCl found.
	Gram.	Gram.	Gram.
(42)	0.1000	0.0192+	0.0210+
(43)	0.1000	0.0142+	0.0160+
(44)	0.1000	0.0054+	0.0072+
(45)	0.1000	0.0110+	0.0127+
(46)	0.1000	0.0050—	0.0018—
(47)	0.1000	0.0017—	0.0008—

From these results it is plain that it is a far more difficult matter
to dehydrate and dissolve calcium chloride than either magnesium
chloride or lithium chloride. The separation of the chlorides of
sodium and potassium from calcium chloride cannot be accom-
plished, for the quantities employed in these experiments, by a
single precipitation; but the repetition of the treatment is effective.

In the residues of Experiments (46) and (47) calcium could not be found by the test with ammonium oxalate. In a case, therefore, in which the separation of sodium and potassium from lithium, magnesium, and calcium in one operation should be desirable, the end may probably be accomplished by means of the process here described.

Certain preliminary experiments with the nitrates of the bases under discussion indicate that these are susceptible of similar separation by the action of amyl alcohol; and the wide applicability in analytical operations of the general principle involved—the dehydrating of salts by means of amyl alcohol or other liquid of high boiling-point and appropriate solvent action—can scarcely be a matter of doubt.

ON ORTHOTOLYLPHTHALIMIDE.

By M. Kuhara.

According to Von Gerichten,[1] it appears probable that phthalyl chloride is either $C_6H_4{<}{CCl_2 \atop CO}{>}O$, or a mixture of this substance with the normal chloride. This led me to consider that phthalyl chloride might yield a substance isomeric with phthalimide by treating the former with ammonia. A few years ago, when in the laboratory of the Johns Hopkins University, working under the direction of Professor Remsen, I made a large number of experiments with the object of testing this idea. In the course of the experiments I obtained only once a substance quite distinct from phthalimide, although isomeric; but all efforts to get possession of this substance again entirely failed, and I was obliged to give up its further study. The details of the experimental results and some account of phthalyl chloride have already been published in this Journal **3,** page 26.

It has since occurred to me that if toluidine instead of ammonia is made to act upon phthalyl chloride, a substance isomeric with tolylphthalimide may probably be produced more readily, and I

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[1] Ber. d. deutsch. chem. Gesell. **13,** 417.

therefore attempted the study of the action of orthotoluidine upon phthalyl chloride.

Action of Orthotoluidine upon Phthalyl Chloride.
Orthotolylphthalimide.

The phthalyl chloride and orthotoluidine used in the experiments were from Kahlbaum, of Berlin, and were purified by fractional distillation. Both substances had the right boiling-points. On mixing them together in the proportion of 1 mol. phthalyl chloride and 1 mol. orthotoluidine and gently warming, a violent reaction took place, with the evolution of hydrochloric acid, and the whole substance soon solidified. After washing the mass successively with water, hydrochloric acid and caustic soda, it was dissolved in alcohol and repeatedly crystallised. During crystallisation I paid a great deal of attention to each crop of crystals, as more than one kind of substance may possibly be formed at the same time. I could not, however, obtain more than one substance, so that phthalyl chloride seems not to be a mixture.

The substance thus obtained consists of groups of snow-white, microscopic short needles. It is insoluble in water, and difficultly soluble in cold alcohol and ether, more readily in hot glacial acetic acid and alcohol. It melts at 182°. The substance, dried at 100°, was analysed :

    I. 0.2972 gram gave 0.8266 gram CO_2 and 0.1271 gram H_2O.

    II. 0.30200 gram gave 0.8400 gram CO_2 and 0.1272 gram H_2O.

    III. 0.2622 gram gave 0.7298 gram CO_2 and 0.1109 gram H_2O.

		Calculated for $C_{15}H_{11}O_2N$.	I.	Found. II.	III.
Carbon,	180	75.95	75.85	75.86	75.91
Hydrogen,	11	4.64	4.75	4.68	4.69
Nitrogen,	14	5.91	…	…	…
Oxygen,	32	13.50	…	…	…
	237	100.00			

This substance is identical with " phthalorthotoluid," obtained by Froehlich[1] by fusing orthotoluidine and phthalic anhydride together, and its structure is represented by one of the two formulas below, depending upon the structure of phthalyl chloride :
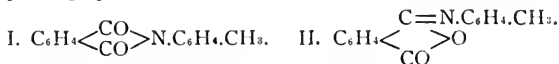
$$\text{I. } C_6H_4{<}^{CO}_{CO}{>}N.C_6H_4.CH_3. \qquad \text{II. } C_6H_4{<}^{C=N.C_6H_4.CH_3.}_{CO}{>}O$$

[1] Ber. d. deutsch. chem. Gesell. **17**, 2673. Inaugural dissertation, Berlin, März, 1885.

The formula I, however, seems to be more probable than II, inferring from the results of experiments which I will describe hereafter, and I therefore call the substance orthotolylphthalimide.
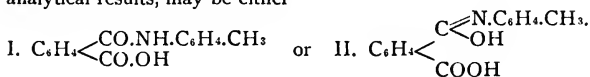
Orthotolylphthalamic Acid.

On boiling orthotolylphthalimide with concentrated aqueous ammonia for a few hours, it gradually dissolved, and after driving off the excess of ammonia by further boiling, dilute hydrochloric acid then added precipitated an acid. The precipitate was dissolved in alcohol, in which it was very soluble, and repeatedly crystallised from the solution.

The acid crystallises in beautiful fine needles. It is soluble in water, more readily in alcohol. Its aqueous solution shows a feeble acid reaction towards litmus paper.

The air-dried acid was analysed and gave the following results:

		Calculated for $C_{15}H_{13}NO_3$.	Found.
Carbon,	180	70.58	70.72
Hydrogen,	13	5.10	5.38
Nitrogen,	14	5.50	...
Oxygen,	48	18.82	...
	255	100.00	

This acid, which I call orthotolylphthalamic acid, is probably identical with "phthalorthotoluidinsäure," described by Froehlich.[1] The constitution of the acid, as far as can be judged from the analytical results, may be either

$$\text{I. } C_6H_4 {\displaystyle {< \atop} {CO.NH.C_6H_4.CH_3 \atop CO.OH}} \quad \text{or} \quad \text{II. } C_6H_4 {< \atop} C {\displaystyle {< \atop} {N.C_6H_4.CH_3 \atop OH}} \atop COOH$$

Normal Lead Orthotolylphthalamate.

This salt was prepared by precipitating with lead acetate from the neutral solution of ammonium orthotolylphthalamate obtained by boiling orthotolylphthalimide with concentrated ammonia, as in the case of the preparation of the free acid. The precipitate, well washed and dried at 100°, was analysed:

I. 0.66 gram gave 0.209 gram Pb.

II. 0.1168 gram gave 0.03716 gram Pb.

[1] Ber. d. deutsch. chem. Gesell. **17**, 2673. Inaugural dissertation, Berlin, März, 1885.

$$\left(C_6H_4{<}^{\mathrm{CONH.C_6H_4.CH_3}}_{\mathrm{COO}}\right)_2 Pb.$$

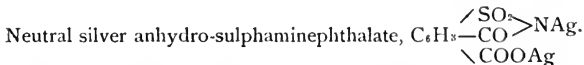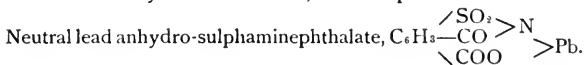|	Calculated for	Found.	
		I.	II.
Lead,	30.13	31.66	31.81

Mono-Lead Orthotolylphthalamate.

This salt was prepared by precipitating with basic lead acetate from the neutral solution of ammonium orthotolylphthalamate. The precipitate, dried at 100°, was analysed:

I. 0.202 gram gave 0.0937 gram Pb.

II. 0.1342 gram gave 0.0622 gram Pb.

III. 0.2100 gram gave 0.0949 gram Pb.

$$C_6H_4{<}^{\mathrm{CO-N-C_6H_4.CH_3}}_{\mathrm{COO}}{>}Pb.$$

	Calculated for		Found.	
		I.	II.	III.
Lead,	45.00	46.38	46.34	45.19

In I and II the amount of lead is a little higher than the theoretical, and this may be due to the formation of lead carbonate with basic lead acetate by the action of air during the precipitation and filtration of the salt. In III the amount of lead almost agrees with theory, and in this case the precipitation and filtration were conducted in an atmosphere of hydrogen in order to prevent the action of carbon dioxide upon the acetate.

Considering the formation of this mono-lead salt, one molecule of orthotolylphthalamic acid seems to contain two atoms of hydrogen replaceable by metal. On inspecting the two possible formulas of the acid represented above, the formula I contains two replaceable hydrogen atoms, of which one is that of carboxyl and the other is that of the imide group. It is well established that the imide hydrogen under some conditions has acid properties. Remsen and Stokes[1] give a list of salts of this kind, and those which were obtained by one of them are, for example:
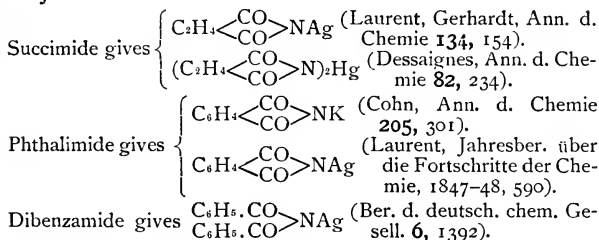
Neutral lead anhydro-sulphaminephthalate, $C_6H_3{-}^{\mathrm{SO_2}}_{\mathrm{CO}}{>}N{>}^{}_{\mathrm{COO}}{>}Pb.$

Neutral silver anhydro-sulphaminephthalate, $C_6H_3{-}^{\mathrm{SO_2}}_{\mathrm{CO}}{>}NAg.$ $_{\mathrm{COOAg}}$

Neutral potassium anhydro-sulphaminephthalate,

$$C_6H_3{-}^{\mathrm{SO_2}}_{\mathrm{CO}}{>}NK.$$
$$_{\mathrm{COOK}}$$

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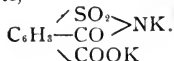
[1] This Journal **6**, 262.

Several other examples of similar salts are found described in the Journals as :

Succimide gives $\begin{cases} C_2H_4{<}^{CO}_{CO}{>}NAg & \text{(Laurent, Gerhardt, Ann. d.} \\ & \text{Chemie } \mathbf{134}, 154). \\ (C_2H_4{<}^{CO}_{CO}{>}N)_2Hg & \text{(Dessaignes, Ann. d. Che-} \\ & \text{mie } \mathbf{82}, 234). \end{cases}$

Phthalimide gives $\begin{cases} C_6H_4{<}^{CO}_{CO}{>}NK & \text{(Cohn, Ann. d. Chemie} \\ & \mathbf{205}, 301). \\ C_6H_4{<}^{CO}_{CO}{>}NAg & \text{(Laurent, Jahresber. über} \\ & \text{die Fortschritte der Che-} \\ & \text{mie, 1847--48, 590).} \end{cases}$

Dibenzamide gives $^{C_6H_5.CO}_{C_6H_5.CO}{>}NAg$ (Ber. d. deutsch. chem. Gesell. $\mathbf{6}$, 1392).

According to the formula II above, the acid possesses only one replaceable hydrogen, because it contains one alcoholic hydroxyl besides one carboxyl group. This hydroxyl group is, no doubt, tertiary alcoholic, and it is very improbable that the hydrogen of alcoholic hydroxyl can be replaced by a metal by treating with bases and metallic salts. It is very likely that orthotolylphthalamic acid and its mono-lead salt have the constitutions represented below :

$$C_6H_4{<}^{CO.NH.C_6H_4.CH_3}_{COOH}, \quad C_6H_4{<}^{CO.N-C_6H_4.CH_3}_{COO}{>}Pb.$$
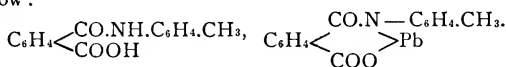
Normal Silver Orthotolylphthalamate.

On adding silver nitrate to the neutral solution of ammonium orthotolylphthalamate prepared by boiling orthotolylphthalimide with ammonia, there was at first produced a white, bulky precipitate of the salt, which soon lessened in bulk and changed to a crystalline form. The precipitate, dried at 100°, was analysed :

I. 0.1134 gram of the salt gave 0.03236 gram Ag.
II. 0.1404 gram of the salt gave 0.04190 gram Ag.
III. 0.1936 gram of the salt gave 0.05940 gram Ag.

	Calculated as $C_6H_4{<}^{CO.NH.C_6H_4.CH_3}_{COOAg}$	I.	Found. II.	III.
Silver,	29.80	28.53	29.84	30.68

Di-Silver Orthotolylphthalamate.

When silver nitrate was added to the neutral solution of the ammonium salt, the white, bulky precipitate at first produced was

quickly filtered by means of a filter-pump before it changed into a crystalline state. The precipitate, dried at 100°, was analysed :

0.322 gram of the salt gave 0.152 gram Ag.

$$\text{Calculated as } C_6H_4{<}{\overset{CON{<}{\overset{C_6H_4.CH_3.}{Ag}}}{COOAg}}$$

		Found.
Silver,	46.04	45.84

Mono-Barium Orthotolylphthalamate.

This salt was prepared by boiling orthotolylphthalimide with pure baryta water. The excess of baryta was removed by means of carbonic acid, and the solution, filtered from barium carbonate, was concentrated. On adding a large excess of strong alcohol to this solution, the salt was precipitated. The precipitate, dried between 90° and 100°, was analysed :

0.1408 gram salt gave 0.084 gram $BaSO_4 = .0493$ Ba.

	Calculated for $C_6H_4{<}{\overset{CON-C_6H_4.CH_3.}{COO{>}Ba}}$	Found.	Calculated for $(C_6H_4{<}{\overset{CONH.C_6H_4.CH_3}{COO}})_2Ba.$
Barium,	35.12	35.01	21.24

Methyl Derivatives of Orthotolylphthalamic Acid.

The object of this experiment was to introduce a methyl group in place of the hydrogen in the imide group of the acid, expecting that if the formula I of the acid is correct, its methyl derivative, by decomposing with alkali, may produce monomethyl toluidine and phthalic acid. The experiment was conducted as follows : Finely pulverised orthotolylphthalamic acid was suspended in xylene, in which the acid partly dissolved, and then metallic sodium added in small pieces, and the whole heated in a flask over a calcium chloride bath for several days, during which the contents of the flask gradually changed into a shining, pasty mass, which was the sodium compound of the acid. An excess of methyl iodide was then added and the whole heated over a water bath. In a few hours the methyl compound was formed and sodium iodide settled to the bottom of the flask. Now, on adding a large quantity of water to the flask and shaking, some metallic sodium still left was converted into sodium hydrate and made the liquid strongly alkaline. The contents of the flask were then subjected to distillation with steam. The distillate, consisting mainly of xylene, was shaken up with dilute hydrochloric acid, and two

layers of liquids produced on standing were separated. By making the aqueous portion alkaline with sodium hydrate, an oil was precipitated, which was purified by distillation. The oil is colorless and smells like toluidine, and soon changes brown in air. It neither gives any characteristic reactions of toluidine nor gives an acetyl compound with either acetyl chloride or acetic anhydride, while toluidine and monomethyl toluidine readily yield acetyl compounds. Although I could not determine the exact boiling point of the substance, as the quantity was not quite enough for experiment, its properties seemed to be identical with those of the dimethyl-orthotoluidine of Thomsen[1] and Nölting.[2] It was then converted into the platinum double salt and several times crystallised from aqueous alcohol for purification. The double salt, dried at 100°, was analysed :

   I. 0.1226 gram of the salt gave 0.0354 gram Pt.

   II. 0.1084 gram of the salt gave 0.0310 gram Pt.

	Calculated as $2C_6H_4{<}{}^{CH_3}_{N(CH_3)_2}HCl + PtCl_4.$	Found. I.	II.
Platinum,	28.99	28.87	28.59

The residual liquid in the flask was concentrated, and on adding hydrochloric acid to it a large quantity of phthalic acid was precipitated. In order to prove its identity it was converted into its potassium salt, which was dried at 100° and analysed :

	Calculated as $C_6H_4(COOK)_2.$	Found.
Potassium,	32.23	32.21

The formation of dimethyl-toluidine and phthalic acid may be explained thus: It is very probable that iodomethylate of orthotolylphthalamic acid would be formed, and that when the contents of the flask are distilled with steam the iodomethylate would be decomposed, as the liquid is strongly alkaline. The decomposition may be represented as follows:

$$C_6H_4{\Big<}{}^{\displaystyle CO-\overset{\displaystyle I\ \ CH_3}{\overset{\vee}{N}}-C_6H_4.CH_3}_{\displaystyle \underset{COONa}{CH_3}} + 2NaHO =$$

$$C_6H_4(COONa)_2 + C_6H_4{<}{}^{CH_3}_{N(CH_3)_2} + NaI + H_2O.$$
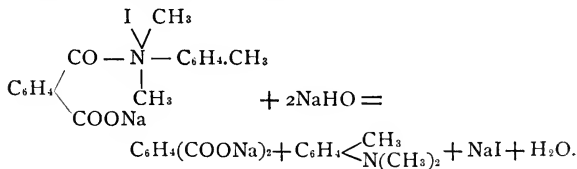
[1] Ber. d. deutsch. chem. Gesell. **10**, 1586.   [2] Ber. d. deutsch. chem. Gesell. **11**, 2279.

In order to confirm the formation of the iodomethylate, I repeated the experiment, which was conducted in the same way as before, by heating orthotolylphthalamic acid suspended in xylene with metallic sodium and methyl iodide. In this experiment xylene and all other soluble substances were extracted with ether, without adding any water to the flask. From the ethereal extract the ether was distilled off, and the residual liquid, consisting mainly of xylene, was distilled, together with water, by which all the xylene was separated. On evaporating the residual liquid to a syrupy consistency, the whole solidified to a semi-crystalline mass. It was found difficult to obtain the substance in a pure state, as it contained a large quantity of sodium iodide, and was little capable of crystallisation. On heating the semi-crystalline mass, it fused, giving a large quantity of methyl iodide, and again solidified. The substance may therefore be iodomethylate of orthotolylphthalamic acid. The substance left after giving off methyl iodide was also not easy to crystallise, so that it was difficult to purify. The substance, which was not pure, was analysed, so that it may throw light on its nature :

$$C_6H_4 < \begin{matrix} CO.N < \begin{matrix} CH_3 \\ C_6H_4.CH_3. \end{matrix} \\ COONa \end{matrix}$$

	Calculated as	Found.	Diff.
Sodium,	9.41	7.9	1.51

In conclusion, I should say, the results of the above experiments can be best explained by assuming that phthalyl chloride has the commonly accepted formula. Further investigations are now in progress.

CHEMICAL LABORATORY, MEDICAL DEPARTMENT,
    UNIVERSITY OF TOKIO, JAPAN, *August* 10, 1886.

MANGANESE IN STEEL AND IRON.

BY H. C. BABBITT.

In various communications which I have read upon those methods of determining manganese in iron and steel which depend upon the oxidation of the manganese to permanganic acid by the

action of lead peroxide in a nitric acid solution, all who do not absolutely condemn seem to agree that the presence of lead nitrate and the time of boiling have a great influence upon the accuracy of the results. A number of years ago I began to use a volumetric method of this description, and the difficulty of obtaining a reasonably pure lead peroxide, and the annoyance of preparing it for myself, led me to try red lead, Pb_3O_4, as an oxidising agent. After numerous experiments, by adding known quantities of manganese to an iron free from that element, and repeated checks by the acetate and other processes, with samples of steel varying from .05 to 2.00 per cent. of manganese, I became convinced of its utility, and for the past six years have used it on all grades of iron and steel, and occasionally upon spiegeleisen, with uniformly good results.

The discussion of this method has led me to make the following experiments, which may be of interest. The sample which I selected was a machinery steel of about .50 carbon, .04 silicon, and .09 phosphorus. The manganese by the acetate of soda and bromine process was obtained with the utmost care, using all possible precautions for accuracy.

By $NaC_2H_3O_2$ and $Br = .515$ per cent. manganese :

	A.	B.	
No. 1.	.516	.512	per cent. of manganese.
2.	.516	.513	
3.	.513	.518	
4.	.518	.518	
5.	.513	.518	
6.	.513	.513	

The method of procedure was as follows : .5 gram of steel was dissolved in about 15 cc. HNO_3 (1.15 to 1.20 sp. gr.), in a 50 cc. beaker. The solution was boiled till nitrous fumes ceased, red lead added—in A, one gram ; in B, two grams. The solution was then diluted to about 30 cc. with hot water. In No. 1 the solution was simply stirred after its addition ; in No. 2, heated to boiling ; No. 3, boiled for one minute ; No. 4, for two and a half minutes ; No. 5, five minutes ; No. 6, fifteen minutes. The solutions were then set aside to allow the residual lead peroxide to settle, the supernatant liquid decanted and the residue boiled with more hot water containing from 20 to 25 per cent. of nitric acid. These decantations are continued as long as they show a decided color of per-

manganic acid. When the manganese is below .60 per cent., one decantation and subsequent boiling is generally sufficient. The combined decantations are then filtered through asbestos and titrated with a standard reducing agent. If the presence of lead nitrate were fatal to accuracy, certainly the use of a compound which, when added to nitric acid, becomes a mixture of lead nitrate and lead peroxide, $2Pb(NO_3)_2 + PbO_2$, would be inadmissible ; and the difference in time between the addition of hot water and boiling for fifteen minutes is an exceptionally wide limit. The only difference which I have ever found between filtering hot and cold is that occasionally lead peroxide will run through the filter and cause too high results from coincident oxidation of the reduced manganese. I have never been able to obtain uniformly accurate results with steel above .50 per cent. of manganese by taking an aliquot portion of the first decantation for titration, while companion analyses treated in the usual manner have yielded results which compared favorably with gravimetric methods.

CHESTER ROLLING MILLS, THURLOW, PA.

METHODS OF BUTTER ANALYSIS.

BY F. W. A. WOLL.

The manufacture of artificial butter has during the last ten years attained vast dimensions both in America and Europe. With the increased manufacture and consumption, the methods of distinguishing between artificial and natural butter have become of greater importance, and the chemist is now frequently called upon to apply them. Of all the methods which have been proposed for chemical analysis of butter, those of Messrs. Reichert and Koettstorfer have found the most general application among American chemists, and they are also the only really practical methods which have thus far been devised. Hehner and Angell's method

is considered too lengthy and impracticable, while Baron Hübl's[1] method, though very good, is yet comparatively new and seems not to have become sufficiently known.

Of the 35,000,000 pounds of artificial butter said to have been manufactured in the United States in 1885, more than half, or nearly 20,000,000 pounds, is stated to have been made in Chicago. The greater part of this amount is called *butterine*, a mixture of oleo oil, neutral oil and natural butter. Butterine is commonly manufactured in two grades, called creamery and dairy butterine. The former contains 25 to 35 per cent., the latter 10 to 15 per cent. of natural butter.

As butterine is very frequently found in the market, samples of it are often sent to the chemist for analysis, and it then becomes desirable to determine the amount of natural butter it contains. This percentage may be calculated by means of the equations given by the authors of the methods mentioned above. To determine how accurately it is possible to determine the true amount of butter in a mixture by analysis according to Koettstorfer's and Reichert's methods, and otherwise to study the subject of butter analysis and artificial butter, the writer has been engaged in researches in this direction since January, 1886. To determine the first point, mixtures of natural butter fat and the crude product called *oleo oil* were made. These, which had both been previously analysed, were weighed out in fluid condition in the required proportions, mixed as well as possible, and then analysed according to the two methods. The following table gives the results :

TABLE I.

Per Cent. Butter.	Koettstorfer.			Reichert.			Per Cent. of Butter Found by							
							Koettstorfer's Method.				Reichert's Method.			
	Calculated.	Found.	Difference.	Calculated.	Found.	Difference.	Highest.	Lowest.	Average.	Difference.	Highest.	Lowest.	Average.	Difference.
	Mgr.	Mgr.		Cc.	Cc.		Per Ct.	Per Ct.	Per Ct.		Per Ct.	Per Ct.	Per Ct.	
20	200.8	201.4	+0.6	2.98	3 11	+0.13	36.3	1.7	18.3	—1.7	21.2	19.8	20.5	+0.5
40	206.2	207.3	+1.1	5.81	6.39	+0.58	55.0	20.4	37.6	—2.4	45.9	43.0	44.5	+4.5
50	208.5	209.0	+0.5	6.55	7.08	+0.53	60.4	25.8	42.9	—7.1	51.1	47.9	49.5	—0.5
60	211.5	212.7	+1.2	8.65	9.06	+0.41	72.1	37.6	54.7	—5 3	67.6	61.8	63.0	+3.9
80	217.7	215.6	—2.1	10.37	11.56	+1.19	81.3	46.7	63.9	—16.1	85.1	79.5	82.2	+2.2
Average			1.1			0.57				6.5				2.3

[1] Dingler, Polyt. Journal **253**, 281 ; also Fresenius' Analytische Zeitschrift **25**, 432.

The difference between the calculated and the observed number of mgrms. and cc. used in the analysis according to the two methods, must be ascribed to the difficulty of getting a perfectly homogeneous mixture. The numbers are averages of two or more determinations. The percentages of butter are calculated after the well-known equations,

$$x = (227 - n) \, 3.17 \text{ and}$$
$$x = (7.30 \pm 0.24) \, (n - 0.3),$$

taking by Koettstorfer's method 232.4, 227 and 221.5 mgrms. as highest, average, and lowest value for genuine butter. The differences between the results calculated from the average numbers and the true percentages of butter are given in the table. In this case, where the butter had a very low value according to Koettstorfer's method (222.2 and 223.2 mgrms.), the difference was quite marked —on an average 6.5 per cent., with a highest value of 16.1 per cent. Reichert's method gives more closely accordant results, the average difference being 2.3 per cent. and highest 4.5 per cent. As will be seen, the method of Reichert gives the amount of genuine butter in a butterine with all desirable accuracy.

The results of analyses of thirty-seven samples of genuine butter, artificial butter and crude products are given below. As it may be of statistical interest, the results of the determinations of specific gravity and melting-point are also given ; the former was determined by a 10 cc. specific gravity bottle at 37.7° C.,[1] and the latter by application of a glass bulb as devised by Hehner and Angell.[2] The weight of the glass bulb used was 3.386 grams.

The samples were obtained partly by direct application to the manufacturers, partly by purchase at grocery stores in Milwaukee, Wis., and Chicago, and partly by sampling on the spot in the manufactory of Armour & Co., Chicago.

TABLE II.

1.—*Genuine Butter.*

No.	Sold as : Price.	Water.	Sp. Gr.	Melting-Point.	Koett-storfer.	Reichert.
3	Creamery Butter........ ..	11.88 per cent.	.91274	34 5° C.	225.0 mgr.	13.05 cc.
15	Dairy Butter...............	,,	.91133	35.0	221.4	13.29
23	" "	,,	.91200	34.0	222.2	14.36

[1] Blyth, Foods, Composition and Analysis, London, 1882, p. 295.

[2] Hehner and Angell, Butter Analysis, p. 22.

2.—*Crude Products.*

8	Oleo Oil I	6.73 per cent.	.90356	29.2° C.	192.0 mgr.	.04 cc.
9	" II (for export.)...	No.	.90354	25.7	191.7	.19
24	"	No.	.90365	29.7	195.3	.03
27	"	..	.90368	27.7	195.0	.12
37	"	..	.90402	25.9	192.9	.08
10	Neutral Oil................	4.67	.90552	37.8	190.8	.03
25	" "	7.49	.90502	38.1	193.7	No.
28	" "	..	.90536	38.3	195.5	.15
36	Sesame Oil..............	..	.91326	.	185.1	.17
22	Cocoanut Oil.............	..	.91743	24.5	257.9	3.64
11	Crude Stearine	No.	.90124 (65° C.)	55.3	193.6	.37

3.—*Commercial Butters.*

1	Suspected Butter..	8.77 per cent.	.91184	35.5° C.	225.5 mgr.	13.33 cc.
16	" "	..	..	..	223.9	12.59
2	" "	..	..	..	230.5	14.69
26*	Butterine.................	..	.90586	35.1	198.7	2.39
29*	Creamery Butter.........	..	.90576	34.5	201.2	2.93
12*	Creamery Butterine.......	11.25	.90554	34.5	202.2	4.43
13*	Dairy Butterine..........	10.39	.90449	33.9	190.4	1.59
14*	Oleomargarine............	9.89	.90526	33.6	190.4	.53
4	Butter, Milwaukee, 24 c.	9.42	.91206	34.3	222 9	14.36
5*	" " 22 c.	14.10	.90604	34.6	193.1	1.54
6*	Butterine, " 20 c.	11.19	.90536	34.0	199.6	3.49
7*	" " 15 c.	13.02	.90440	32.0	194.2	2.16
17	Best Cr'y, Chicago, 35 c.	..	.91213	34.4	223.4	14.03
18	Fancy Dairy, " 30 c.	..	.91107	33.8	223.2	12.92
19*	" " " 22 c.	..	.90502	33.2	195.4	1.57
20*	Dairy No. 1, " 16 c.	..	.90574	32.5	197.3	.62
21	Best Cr'y, " 35 c.	..	.91117	33.0	222.4	13.41
30*	Dairy, " 20 c.	..	.91008	34.2	216.3	11.94
31*	Best Cr'y, " 30 c.	..	.90504	36.1	197.1	1.29
32	Best Dairy, " 25 c.	..	.91166	36.5	232.0	14.02
33*	Elgin Cr'y, " 23 c.	..	.90546	32.8	202.9	2.70
34	Good Cr'y, " 25 c.	..	.91120	32.0	222.3	13.78
35	Good Dairy, " 20 c.	..	.91166	32.3	226.2	14.28

NOTE.—* Artificial butter.

Genuine butter: Sp. gr. 0.914–0.91100, m.-point 32.0–36.5° C.; Koettstorfer: 221.4–232.4 mgr.; Reichert: 12.0–14.9 cc.

The samples No. 8–14 and 36 were from the manufactory of Armour & Co.; No. 24–26 from Fitts & Co.; No. 27–29 from Wm. J. Moxley; No. 37 from Fairbank Canning Co., all of Chicago. No. 3 was sent, on request, from Polar Creamery, Houston, Minn., firm Hostvet & Hourn. The suspected samples were sent to this station for analysis by private parties.

The three samples of genuine butter were pure beyond doubt. The samples are given the names under which they were sold. Out of eleven samples of butter bought at Chicago grocery stores at random, five were artificial butter. As will be seen, the determination of the melting-point is of no use in discriminating between a natural and an artificial butter. The specific gravity and Koettstorfer's or Reichert's methods, on the other hand, either singly or in combination, are decisive.

Oleo oil, neutral oil and sesame oil are used in the manufacture of artificial butter; oleo oil, made from the caul fat or the kidney

fat of beeves, has, on an average, specific gravity 0.90369; melting point, 27.6° C.; by Koettstorfer's method it requires 193.4 mgrms. KOH, and by Reichert's method .09 cc. deci-normal NaOH solution. Neutral oil, made from the leaf lard of hogs, has a specific gravity of 0.90530; melting-point, 38.1° C.; Koettstorfer's method requires 193.3 mgrm. KOH, and by Reichert's 0.16 cc. deci-normal NaOH solution. The specific gravity of genuine butter is usually considered to range from 0.91400 to .91200; seven of the eleven samples of genuine butter reported on above had a lower specific gravity than this limit. The lowest result was 0.91107.

The samples of artificial butter which were not oleomargarine— *i. e.* prepared only from oleo oil, neutral oil and a little cream or milk—contained butter in the following percentages, approximately:

No. 6,	20 per cent.	No. 26,	15 per cent.
" 7,	10	" 29,	20
" 12,	30	" 30,	80
" 13,	10	" 31,	10
" 19,	10	" 33,	20

The sample No. 30, containing 80 per cent. of natural butter, must have originated in some creamery, and would be more properly called adulterated butter; it would not pay for a manufacturer of artificial butter to use such a quantity of butter. As a rule, not more than 50 per cent. of pure butter enters the artificial product.

ESTIMATIONS OF CARBONIC ACID IN THE AIR.

By THOMAS C. VAN NÜYS AND BENJAMIN F. ADAMS, JR.

During the month of April, 1886, we made eighteen estimations of carbonic acid in the air, employing Van Nüys' apparatus, described in this Journal **8,** 190. These estimations were made in the University Park, one-half mile from the town of Bloomington. The park is hilly, thinly shaded, and higher than the surrounding country. The formation is sub-carboniferous and altitude 228 metres. There are no lowlands or swamps in the vicinity. The estimations were made at 10 A. M.

The air was obtained one-half metre from the ground and about 100 metres from any of the University buildings. The number of volumes of carbonic acid is calculated at zero C. and normal pressure 760 mm.

Date.		Bar. Pressure.	Vols. CO_2 in 100,000 Vols. Air.	State of Weather.
April	2	743.5	28.86	Cloudy, snow on ground.
"	5	743.5	28.97	" " " "
"	6	735	28.61	Snowing.
"	7	741.5	28.63	Clear, snow on ground.
"	8	748	27.59	" thawing.
"	9	747.5	28.10	" "
"	12	744	28.04	Cloudy.
"	13	744	28.10	Clear.
"	14	743.5	28.98	"
"	15	750.5	28.17	Raining.
"	19	748	28.09	Clear.
"	20	746	27.72	"
"	21	746	28.16	"
"	22	741.5	27.92	"
"	23	740	28.12	"
"	24	738.5	28.15	"
"	25	738.5	27.46	"
"	28	738	27.34	"

The average number of volumes of carbonic acid in 100,000 volumes of air is 28.16, the maximum number is 28.98, and the minimum 27.34. These results agree with estimations made within the last ten or fifteen years. Reiset[1] made a great number of estimations from September 9, 1872, to August 20, 1873, the average of which is 29.42. Six years later[2] he made many estimations from June to November the average of which is 29.78. The average of Schultze's[3] estimations is 29.2. The results of estimations of carbonic acid in the air, made under the supervision of Münz and Aubin[4] in October, November and December, 1882, at the stations where observations were made of the transit of Venus by astronomers sent out by the French Government, yield the average, for all stations north of the equator to latitude 29° 54′ in Florida, 28.2 volumes carbonic acid in 100,000 volumes air, and for all stations

[1] Comptes Rendus **88**, 1007.   [2] Comptes Rendus **90**, 1144.
[3] Chem. Centralblatt, 1872 and 1875.   [4] Comptes Rendus **96**, 1793.

5

south of the equator 27.1 volumes. The average of Claesson's[1] estimations is 27.9 volumes, his maximum number is 32.7, and his minimum is 23.7. It is apparent, from the results of estimations of carbonic acid of the air of various parts of the globe, by the employment of apparatus with which errors are avoided, that the quantity of carbonic acid is subject to slight variation, and not, as stated in nearly all text-books of science, from 4 to 6 volumes in 10,000 volumes of air; and it is further apparent that the law of Schloesing[2] holds good. By this law the carbonic acid of an atmosphere in contact with water containing calcium or magnesium carbonate in solution is dissolved according to the tension of the carbonic acid; that is, by an increased quantity its tension increases and more would pass in solution in the form of bicarbonates. On the other hand, by diminishing the quantity of carbonic acid in the atmosphere, some of the bicarbonates would decompose and carbonic acid pass into the atmosphere.

Schloesing's law has been verified by R. Engel.[3]

The results of estimations of bases and carbonic acid in the water of the English Channel lead Schloesing[4] to conclude that the carbonic acid combined with normal carbonates, forming bicarbonates, dissolved in the water of the globe is ten times greater in quantity than that of the atmosphere, and on account of this available carbonic acid, if the atmosphere should be deprived of some of its carbonic acid, the loss would soon be supplied.

As, in nearly all of the methods which were employed for estimating carbonic acid in the air, provision is not made for the exclusion of air not measured containing carbonic acid from the alkaline fluid before titrating or weighing, the results are generally too high and show a far greater variation than is found by more exact methods; for example, Gilm[5] found from 36 to 48 volumes; Levy's[6] average is 34 volumes; De Luna's,[7] 50 volumes; and Fodor's,[8] 38.9 volumes. Admitting that the quantity of carbonic acid in the air is subject to variation, yet the results of Reiset's and Schultze's estimations go to prove that the variation is within narrow limits.

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　　　　　　　　　　　　BLOOMINGTON, INDIANA.

[1] Berichte der deutsch. chem. Gesellschaft **9,** 174.　　[2] Comptes Rendus **74,** 1552 and **75,** 70.
[3] Comptes Rendus **101,** 949.　　　　　　　　　　　[4] Comptes Rendus **90,** 1410.
[5] Sitzungsber. d. Wien. Akad. d. Wissenschaften **34,** 257.
[6] Ann. d. l'Observ. d- Mountsouris, 1878 and 1879.
[7] Estudios quimicos sobre el aire atmosférico, Madrid, 1860.　　　[8] Hygien. Untersuch. **1,** 10.

ON THE ACTION OF SULPHUROUS ANHYDRIDE ON BENZENE.

By Charles E. Colby and C. S. McLoughlin.

When benzene is treated with sulphuric anhydride, the elements of water are eliminated and a compound is formed containing the group SO_2 attached to two phenyl radicles. This body, first prepared by Mitscherlich,[1] was called by him sulpho-benzid ; more recent investigators have given it the name of diphenyl-sulphone. It occurred to the authors that an analogous reaction might be possible between benzene and sulphurous anhydride, thus giving rise to a body containing the group SO combined with two phenyl radicles.

Benzene dissolves sulphurous anhydride in large quantity, but no reaction takes place between them unless condensing agents are present. Friedel and Crafts[2] found that a mixture of benzene and aluminium chloride absorbs sulphurous anhydride with great energy, forming benzene-sulphinic acid. They explain the reaction thus :

$$C_6H_6 + Al_2Cl_6 = C_6H_5Al_2Cl_5 + HCl,$$
$$C_6H_5.Al_2Cl_5 + SO_2 = C_6H_5SO_2Al_2Cl_5.$$
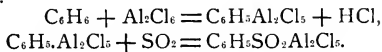
They then add water and thus obtain benzene-sulphinic acid :

$$C_6H_5SO_2Al_2Cl_5 + H_2O = C_6H_5.SO.OH + Al_2Cl_5OH.$$

We repeated these experiments, and, after several trials, proceeded in the following manner :

One hundred grams of benzene and 35 grams of aluminium chloride were placed in a flask fitted with a return condenser. The flask was heated on a water bath and a stream of sulphurous anhydride was passed through it by means of a tube dipping below the surface of the benzene. The sulphur dioxide was rapidly absorbed, the aluminium chloride gradually dissolved, and hydrochloric acid gas escaped. The operation was continued as long as the sulphurous anhydride appeared to be absorbed. The current of the anhydride was then stopped, but the flask was heated till no more hydrochloric acid gas was evolved. The contents of the flask were

[1] E. Mitscherlich, Liebig's Annalen der Chemie **12**, 208.

[2] Friedel and Crafts, Jahresbericht über die Fortschritte der Chemie, Giessen, 1878, 739.

allowed to cool and then poured into cold water. The precipi-
tated aluminium hydrate was then dissolved and washed away by
means of caustic soda. There remained a light yellow oil, which
was separated from the aqueous liquid, dried with calcium chloride,
and then allowed to evaporate at a gentle heat. The excess of
benzene being thus removed, there was left a dirty yellow crystal-
line substance. This, when dissolved in xylene and left to itself,
deposited small, transparent, isolated crystals, apparently belonging
to the triclinic system. They were of a yellowish, waxy color, but
on recrystallisation from petroleum ether they became perfectly
white. Their melting-point lies between 70° and 71°; they are
easily soluble in alcohol, ether, glacial acetic acid and benzene;
difficultly soluble in cold petroleum ether, more readily in hot.

An ultimate analysis furnished the following results:

I. 0.2039 gram substance gave 0.5318 gram CO_2 and 0.0957
gram H_2O.

II. 0.2502 gram substance gave 0.6540 gram CO_2 and 0.1164
gram H_2O.

III. 0.1689 gram substance gave 0.1907 gram $BaSO_4$.

Collecting these figures:

	I.	II.	III.	Theory for $(C_6H_5)_2SO$.
C	71.13	71.28	...	71.286
H	5.21	5.16	...	4.950
S	...	...	15.51	15.843
O	...	...	...	7.921
				100.000

A portion of the substance was dissolved in ten times its weight
of glacial acetic acid and oxidised by adding the calculated quan-
tity of potassium permanganate. After diluting with water, and
crystallising the resulting precipitate from alcohol, there were
obtained white crystalline plates of diphenyl-sulphone melting at
128°. The yield was almost theoretical. Another portion of
the substance on treatment with two molecules of metallic sodium
furnished diphenyl-sulphide boiling at 272°. These results lead
us to the conclusion that the body produced by the action of sul-
phurous anhydride on benzene in presence of aluminium chloride
is diphenyl-sulphoxide, $C_6H_5 — SO — C_6H_5$.

We have also tried the action of thionyl chloride, $SOCl_2$, on

benzene in presence of aluminium chloride. The reaction is represented thus :

$$2C_6H_6 + SOCl_2 = (C_6H_5)_2SO + 2HCl,$$
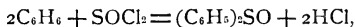
and is analogous to that of oxy-chloride of carbon (phosgene) on benzene in presence of aluminium chloride.

In preparing diphenyl-sulphoxide by means of thionyl chloride we proceeded as follows :

Fifty grams of benzene and 16 grams of thionyl chloride were placed in a flask fitted with a return condenser, the flask being immersed in cold water. Aluminium chloride was then added, in small portions, to the mixture in the flask. The aluminium chloride was rapidly dissolved and hydrochloric acid gas escaped. The addition of aluminium chloride was continued at intervals as long as hydrochloric acid gas was given off. Altogether 30 grams of aluminium chloride were used. Toward the end of the operation 20 grams more of benzene were added to make the mixture more fluid. When fresh addition of aluminium chloride produced no further evolution of hydrochloric acid gas, the flask, with its return condenser still attached, was heated on a water bath for half an hour, then allowed to cool and the contents poured into cold water. A thick yellow oil resulted which floated. This oil was washed with water and then gently warmed in a dish to remove surplus benzene. On cooling there remained a yellowish, waxy mass, which when crystallised from petroleum ether furnished white crystals of the same form as those described above and possessing the same properties. Their melting-point was 70.5°. The ultimate analysis of these crystals showed the same composition as those obtained by the action of sulphurous anhydride on benzene :

I. 0.2500 gram substance gave 0.6523 gram CO_2 and 0.1117 gram H_2O.

II. 0.1000 gram substance gave 0.1160 gram $BaSO_4$.

	I.	II.	Theory for $(C_6H_5)_2SO$.
C	71.16	...	71.286
H	4.96	...	4.950
S	...	15.93	15.843
O	...	...	7.921
			100.000

From 50 grams of benzene and 16 grams of thionyl chloride we

obtained 21 grams of the pure diphenyl-sulphoxide. The theoretical yield is a little more than 26 grams.

It is interesting to note that the diphenyl-sulphoxide fills a gap between the sulphide and sulphone, just as phenyl-sulphinic acid is intermediate between the sulphhydrate and the sulphonic acid :

$\left.\begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\right\}$ S Diphenyl-Sulphide. $\left.\begin{array}{c} C_6H_5 \\ H \end{array}\right\}$ S Phenyl-Sulphhydrate.

$\left.\begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\right\}$ SO Diphenyl-Sulphoxide. $\left.\begin{array}{c} C_6H_5 \\ HO \end{array}\right\}$ SO Phenyl-Sulphinic Acid.

$\left.\begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\right\}$ SO$_2$ Diphenyl-Sulphone. $\left.\begin{array}{c} C_6H_5 \\ HO \end{array}\right\}$ SO$_2$ Phenyl-Sulphonic Acid.
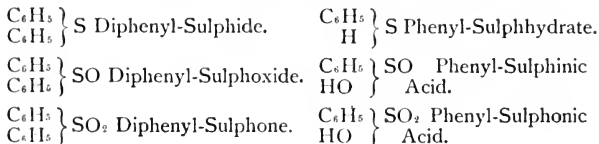
Nitration of the Diphenyl-Sulphoxide.

This operation appears to be difficult, since the nitric acid exerts an oxidising influence on the diphenyl-sulphoxide. The calculated quantities of diphenyl-sulphoxide and of sodium nitrate were dissolved in separate portions of concentrated sulphuric acid. The two solutions were then mixed together and the mixture heated on a water bath for two hours. The mixture was then poured into cold water, and the resulting yellow precipitate, after washing, was dissolved in alcohol and allowed to crystallise. By repeated fractional crystallisation the result of the nitration was separated into three products. *First:* Light yellow crystals, consisting of small rhombic plates, only slightly soluble in alcohol, easily soluble in glacial acetic acid. They had a melting-point of 163°, and we think they are the dinitro-sulpho-benzid described by Gericke.[1] *Second:* Yellow, indistinct, microscopic crystals melting at 116° and readily soluble in cold alcohol, very soluble in ether, benzene, glacial acetic acid and carbon disulphide. Ultimate analysis furnished the following data, showing that it is the dinitrocompound of diphenyl-sulphoxide :

I. 0.2504 gram substance gave 0.4552 gram CO$_2$ and 0.0691 gram H$_2$O.

II. 0.2505 gram substance gave 0.4532 gram CO$_2$ and 0.0677 gram H$_2$O.

III. 0.0500 gram substance gave 0.0401 gram BaSO$_4$.

IV. 0.2000 gram substance gave 18 ccm. nitrogen measured at 30°, and 765.6 mm. corresponding to 0.01966 gram nitrogen.

[1] Gericke, Liebig's Annalen der Chemie, 100–211.

	I.	II.	III.	IV.	Theory for Dinitro-Diphenyl-Sulphoxide. $(C_6H_4NO_2)_2SO$.
C	49.57	49.34	...	...	49.31
H	3.06	3.00	...	...	2.75
S	...	...	11.01	...	10.95
N	...	...	...	9.83	9.59
O	...	...	...	...	27.40
					100.00

The third product of the nitration of diphenyl-sulphoxide seems to be an oil at ordinary temperatures. We have not yet determined its composition or its properties.

We reserve for a future article the results of our work on other substitution derivatives of the diphenyl-sulphoxide, and also on some of its condensation-products.

ORGANIC LABORATORY, SCHOOL OF MINES,
    COLUMBIA COLLEGE, NEW YORK, *November*, 1886.

NOTES.

Germanium.

This new element, which is exciting considerable attention among chemists, was discovered by Clemens Winkler, of Freiburg, in the early part of the year 1886. The constant error of about six per cent. in the result of his analysis of a comparatively simple mineral led him to suspect the presence of one or more new elements.

Such a suspicion was well founded, and, as the result of an exceedingly careful and painstaking investigation, he succeeded in isolating a new substance, which conducts itself in every way like an element; and, what is of still more general interest, a careful study of this new simple body and the compounds which it forms with other elements shows, it can be said almost conclusively, that it agrees in properties with the *eka-silicium* of Mendelejeff.

The silver ore from which germanium is obtained, and which is now known in mineralogy as argyrodite, is found in the neighborhood of Freiburg, and the analysis of the mineral has shown it to have the composition represented by the formula $3Ag_2S,GeS_2$. According to this, it may be regarded as a sulpho-salt for which mineralogy furnishes no analogues.

In order to extract germanium, the mineral in which it occurs is fused with an equal weight of a mixture of equal parts of flowers of sulphur and soda ash ; the fused mass is then boiled with caustic soda, and the solution thus obtained is neutralised with dilute sulphuric acid ; this is then filtered ; to the filtrate dilute sulphuric acid is again added, when the sulphide of germanium is thrown down. This is filtered off and washed with dilute acid containing hydrogen sulphide ; and finally, by treating the washed precipitate with strong nitric acid and evaporating to dryness, germanium oxide is obtained, which may be reduced either by heating to redness in a current of hydrogen, or by heating a mixture of the oxide and starch in a covered crucible. In this way germanium is obtained in the form of a dark gray powder, which melts under borax glass at 900° C.

The element is found to be extraordinarily brittle, and to have a strong tendency to crystallise in the regular system. It has a fine metallic lustre ; in color it is grayish-white, considerably whiter than zirconium. At 20.4° C. it has been found to have a specific gravity of 5.469.

Germanium is not acted on by hydrochloric acid, but is easily dissolved in aqua regia. Nitric acid converts it into a white oxide with liberation of the oxides of nitrogen. Treated with concentrated sulphuric acid, it yields a white, crystalline sulphate, sulphur dioxide being liberated in a constant stream during the action. It is not acted on by potassium hydroxide in the cold.

The atomic weight of germanium has been determined by two entirely different methods : 1st, volumetrically, by determining the amount of chlorine in the tetra-chloride, $GeCl_4$, according to the method of Volhard ; and, 2d, from calculations based on the wave lengths of certain lines in the spark-spectrum. By the former method the atomic weight has been found to be 72.32 ; by the latter 72.28. The very close agreement of this number 72.28, as representing the atomic weight of the new element, with that of the unknown element between gallium and arsenic on the one hand and titanium and zirconium on the other, in the table of Mendelejeff, has naturally led to a very careful comparison of the properties of germanium with those of eka-silicium, whose properties were predicted by Mendelejeff as early as 1871. The results of the comparison will be best seen by presenting them in tabular form :

Eka-Silicium, Es.	*Germanium, Ge.*
Atomic weight, about 72.	Atomic weight, 72.32 and 72.28.
Density, 5.5.	Density, 5.469.
Atomic volume, 13. nearly.	Atomic volume, 13.25.
Will form an oxide, GeO_2.	Forms an oxide, GeO_2.
Sp. gr., 4.7.	Sp. gr., 4.703.

Eka-Silicium, Es.

Easily obtained by reduction with carbon or sodium.

A dirty gray metal, fusible with difficulty, forming the oxide when heated in air.

Will form a chloride of the composition $EsCl_4$, which will boil near 100° C., probably lower. EsO_2 will form a hydrate soluble in acids. This solution will probably decompose readily, yielding an insoluble hydrate.

The sulphide will be insoluble in water, but probably soluble in ammonium sulphide.

The metal will decompose steam very slowly, be scarcely acted on by acids, but easily by alkalies.

It will form volatile organometallic compounds, and will occur in minerals containing titanium and niobium.

According to L. Meyer this element will be:

 Easily fusible,
 Volatile,
 Electro-negative,
 Brittle.

Germanium, Ge.

Easily obtained by reduction with carbon or hydrogen.

A gray-white metal, fusing at 900° C., and forming the oxide when heated in air.

Forms a chloride having the composition $GeCl_4$, which boils at 86° C.

The sulphide is moderately soluble in water, more readily soluble in ammonium sulphide and the alkalies.

Not acted on by hydrochloric acid. Soluble in aqua regia. Nitric acid converts it into the oxide. Sulphuric acid gives the sulphate with liberation of sulphur dioxide. Not acted on by a concentrated solution of potassium hydroxide, but violently by the molten hydroxide.

Occurs in a silver ore of the composition $3 \ Ag_2S, GeS$.

 Fuses at 900° C.,
 Easily volatile,
 Probably electro-negative,
 Very brittle.

A comparison like this shows that we have here to deal with a case similar to that which presented itself when gallium and scandium were discovered, and shown to be identical with eka-aluminium and eka-boron respectively; and a careful consideration of the results already obtained seems to show that, in all probability, the eka-silicium of Mendelejeff and the germanium discovered by Winkler are the same elements. — (*Journal für prak. Chemie* **34,** 177.)   J. H. K.

Inosite.[1]

This substance was first obtained by Scherer from muscular tissue, and has since been found to be a constituent of a large number of plants. The difficulty of obtaining it in any quantity has hitherto prevented its exact study. M. Maquenné has succeeded in obtaining a considerable quantity of it by extracting dried leaves of the walnut tree with water, and has subjected it to careful investigation. He finds that it has the composition represented by the formula $C_6H_{12}O_6 + 2H_2O$; and a determination of its molecular weight by the cryoscopic method of Raoult is also found to be in accord with this formula. It is optically inactive and suffers no change when left in contact with *Penicillium glaucum*. Its molecule, hence, cannot contain an asymmetric carbon atom according to the rule of Le Bel and van't Hoff. Inosite is not attacked by acids nor dilute alkalies. It does not reduce Fehling's solution, nor does it act upon an ammoniacal silver solution. With acid sodium sulphite it does not unite, nor is it reduced by sodium amalgam. The halogens do not act upon it in the cold, but when it is heated with bromine to 100° C. it yields oxidation products similar to those obtained with nitric acid. Inosite is not an aldehyde nor an acetone, since it does not give, on oxidation, an acid containing six atoms of carbon, nor oxy-acids of the fatty series. Its molecule then cannot contain a lateral chain, and it must therefore be a hexatomic alcohol derived from hexahydro-benzene—*i.e.* hexahydro-hexoxy-benzene, $C_6H_6(OH)_6$. The symmetry of this formula excludes, according to the theory of Le Bel and van't Hoff, all rotary power. In another paper,[2] Maquenné shows that, by reduction with hydriodic acid, anhydrous inosite yields a small quantity of benzene and tri-iodophenol—a fact which lends strong support to the formula proposed by him. On oxidising inosite with concentrated nitric acid, he obtained oxy-quinones, such as tetraoxy-quinone, rhodizonic acid, triquinone and croconic acid, all of which have been previously obtained by Nietzki and Benckiser from hexoxy-benzene $C_6(OH)_6$. Hence inosite has the structure represented by the hexagonal symmetrical formula above given, since it yields, both on oxidation and reduction, derivatives of benzene. W. R. O.

[1] Comptes Rendus **104**, 4, 225.   [2] *Ibid.* **104**, 5, 297.

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XLVIII.—ON THE DIRECT CONVERSION OF ARO-MATIC SULPHONATES INTO THE CORRE-SPONDING AMIDO COMPOUNDS.[1]

By C. Loring Jackson and John F. Wing.

The action of sodium or potassium amide on organic substances has been studied but little; in fact, when we took up the subject, there were no papers more recent than those of Beilstein and Geuther[2] on sodium amide in 1858, and of Baumert and Landolt[3] on potassium amide in 1859. The reason for this neglect may be found probably in the curious observation made in both of these papers, that the alkaline amides are not acted on in the way which we should expect by most haloid organic compounds, neither ethyl chloride nor iodide, nor chlorbenzol nor acetyl chloride, giving the corresponding amido compounds;[4] in fact, benzoyl choride is the only haloid organic compound tried which acted as would be

[1] From the Proceedings of the American Academy of Arts and Sciences. Communicated by the authors.   [2] Ann. Chem. 108, 88.   [3] *Ibid.* 111, 1.

[4] These results, so far as the ethyl compounds are concerned, have been confirmed recently by J. Walter, who, in a paper (Journ. pr. Chem. 34, 132) drawn out by the preliminary notice of our work, states that at low temperatures no ethylamine is formed from ethyl bromide; but by heating the sodium amide until it begins to melt, and passing over it a stream of hydrogen impregnated with ethyl bromide, ethylamine was formed, recognised by the carbylamine re-action. Under similar conditions brombenzol gave small quantities of aniline. He, however, does not consider it proved that the amine was formed from the sodium amide, rather than from the ammonia set free during the reaction.

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expected, giving benzamide and dibenzamide. Accordingly, in taking up the subject, we have turned our attention to the effect of sodium amide on sulphonates, in the hope of obtaining an action similar to the well-known replacements of the sulpho-group by hydroxyl, cyanogen, or carboxyl, when fused with potassic hydrate, cyanide, or formiate respectively. This expectation has been fulfilled, as by heating potassic benzolmonosulphonate with sodium amide we have obtained aniline, and in the same way metaphenylenediamine from potassic benzolmetadisulphonate ; but, unfortunately, the yield, especially in the latter case, is so small that the method could hardly be used with profit for the preparation of new amido compounds, so that its usefulness must be confined to determinations of constitution.

The sodium amide was prepared according to the method of Beilstein and Geuther—that is, passing dry ammonia gas over sodium heated in a series of small flasks—except that after the first experiment we dispensed with the use of hydrogen for expelling the air from the flasks before the sodium was heated, using the ammonia gas itself for that purpose.

Action with Potassic Benzolmonosulphonate.—One of the flasks containing the sodium amide was broken, its contents pulverised as rapidly as possible, and mixed (without separating the powdered glass from the flask) with anhydrous potassic benzolmonosulphonate in about the proportion of one molecule of each, calculated from the amount of sodium used in making the amide. The mixture was then heated gently over the lamp in a test tube until the brown fused spots which appear at first had spread throughout the entire mass ; but the process should be stopped before these spots show signs of decomposition, as, if the heat is carried too high, the yield is not so large. During the heating some aniline vapor escapes, but the amount of this is so insignificant that it is not worth while to carry on the process in a retort. The product was then carefully treated with water, and distilled with steam as long as anything passed over. The presence of aniline in the turbid distillate was determined by its smell, by the strong purple color which the distillate gave with a solution of bleaching-powder, and by the analysis of the chloride made by adding dilute hydrochloric acid to the distillate, filtering and evaporating to dryness.

0.4966 gram of the salt gave 0.554 gram of argentic chloride.

	Calculated for $C_6H_5NH_3Cl$.	Found.
Chlorine	27.41	27.60

The yield varied a great deal, but was in the neighborhood of 10 per cent., rising once as high as 15 per cent. of the theory. The portion of the distillate insoluble in dilute hydrochloric acid consisted of white scales, which, after repeated recrystallisation from ligroine, melted between 53° and 54°, and gave an intense blue color with strong nitric acid. We therefore inferred that they consisted of diphenylamine, an inference confirmed by the analysis of the chloride prepared by the action of strong hydrochloric acid and alcohol on the substance, which gave the following result :

0.1334 gram of the salt gave 0.0916 gram of argentic chloride.

	Calculated for $(C_6H_5)_2NH_2Cl$.	Found.
Chlorine	17.27	16.97

The formation of diphenylamine by this reaction would seem to show that the sodium amide used by us was a mixture of $NaNH_2$ with Na_2NH, whereas Beilstein and Geuther proved that the formula of their sodium amide was $NaNH_2$. The explanation of this difference probably can be found in the fact that our amide still contained an excess of sodium, the flasks used by us not being made of a sufficiently resistant glass to allow us to carry the reaction to an end, while in their experiments all the sodium was converted into the amide. It is also possible, but not probable, that the diphenylamine was formed by a secondary reaction from the aniline.

Some experiments to determine the temperature at which the reaction takes place showed that some amine was obtained at 280°, and the yield was not improved at 300°–350° ; but that a much better result was reached by heating over the free lamp than with an oil or air-bath, the products at the temperatures given above amounting respectively to 6.8 and 5.4 per cent. of the theoretical, or about one-half of the amount obtained by the more rapid direct heating over the lamp.

Action of Potassic Benzolmetadisulphonate.—The salt, mixed with about the equivalent amount of sodium amide, was heated in a test tube as before ; but it was found necessary in this case to continue the heating until the brown spots which formed at first had turned black and showed signs of decomposition, since, if the action was stopped while they were still brown, as in the case of the monosulphonate, the yield was exceedingly small. At best,

the yield was not satisfactory, reaching at the outside five per cent. of the theory, so that we did not attempt to collect enough of the tolerably unstable chloride of the metaphenylenediamine for analysis, but contented ourselves with proving its presence by qualitative tests. For this purpose, the product of the reaction was cautiously treated with water, and the aqueous solution extracted with ether; one portion of the ether extract was shaken with dilute sulphuric acid, and to the acid solution thus obtained a very minute amount of sodic nitrite was added, which turned it yellow; another portion of the ether extract was shaken with dilute hydrochloric acid, the acid solution evaporated to dryness, and the residue redissolved in water, filtered from brown decomposition products, and treated with a solution of sodic nitrite, when a heavy, reddish-brown precipitate of phenylene brown was formed; finally, another portion of the ethereal solution of the base was treated with a solution of the nitrate of diazobenzol, when a red, crystalline precipitate was formed, which turned yellow upon the addition of ammonic hydrate, and was therefore the nitrate of chrysoidine. All these tests indicate the presence of metaphenylenediamine in the product of the action of sodium amide upon the potassic benzolmetadisulphonate. The small yield is undoubtedly due to decomposition of a portion of the diamine at the comparatively high temperature necessary for the reaction, as there was a large amount of tarry matter always associated with the product.

XLIX.—ON BENZYLDIMETHYLAMINE.

By C. Loring Jackson and John F. Wing.

At the beginning of the last academic year we prepared the benzyldimethylamine with the intention of making an extended research on this substance; but as the carrying out of this research has been indefinitely postponed on account of the pressure of other more interesting work, we have thought it proper to publish the results already obtained, consisting of the preparation and properties of the base and some of its salts, for the benefit of any one who may follow us in this line of research, rather than on account of any especial interest in the results themselves.

The benzyldimethylamine has been already obtained by Schotten,[1] as one of the products of the distillation of the free base derived from the addition product of methylbenzylpiperidine and methyliodide; but he contented himself with the determination of its presence by the analysis of its chlorplatinate.

Benzyldimethylamine.—To prepare the substance an alcoholic solution of dimethylamine was made by the decomposition of nitrosodimethylaniline, according to the method of Baeyer and Caro,[2] the gas being passed into absolute alcohol, and this was allowed to stand for some hours with benzylchloride. At the end of this time the reaction, which was accompanied with evolution of heat, was finished; and after distilling off the alcohol on the waterbath, the product was treated with water, and then with hydrochloric acid, after which it was extracted with ether to remove a slight non-basic impurity. The base was then set free with sodic hydrate, extracted with ether, washed in the ethereal solution, dried with potassic hydrate, and purified by distillation after driving off the ether. The aqueous liquid, from which the base was extracted with ether, contains the excess of dimethylamine, and the chloride of dibenzyldimethylammonium, the extraction of which will be described later in this paper.

Properties of the Benzyldimethylamine.—It forms a colorless liquid with a peculiar smell, boiling at $183°$–$184°$[3] with the column entirely in the vapor and the barometer at 76.53 cm. It is insoluble in water, but mixes freely with alcohol or ether. Two attempts to convert it into a nitroso-compound gave negative results.

The *chloride* is deliquescent, and forms white, radiating crystals.

The *nitrate* is also deliquescent, so that crystals can be obtained only with difficulty; it forms slender white needles, with many shorter ones crossing them at right angles.

The composition of the base was determined by the analysis of its chlorplatinate and acid ferrocyanide.

Chlorplatinate, $[C_7H_7(CH_3)_2N]_2H_2PtCl_6$.—The salt was prepared by adding chlorplatinic acid to the free base, purified by crystallisation from water, dried at $100°$, and analysed.

[1] Berichte d. deutschen chem. Gesellschaft **15**, 424.

[2] *Ibid.* **7**, 963.

[3] This determination of the boiling-point was made with too small a quantity of the substance, and must be considered as merely approximate. If we had continued the research, we should have repeated it on a more satisfactory scale.

I. 0.2288 gram of the salt left on ignition 0.0656 gram of platinum.

II. 0.3320 gram left 0.0944 gram of platinum.

III. 0.3994 gram left 0.1148 gram of platinum.

IV. 0.4244 gram left 0.1216 gram of platinum.

	Calculated for $[C_7H_7(CH_3)_2N]_2H_2PtCl_6$.	I.	II.	Found. III.	IV.
Platinum	28.63	28.67	28.43	28.74	28.65

Properties.—The appearance of the substance varied a great deal, according to the conditions under which the crystals were obtained ; thus, we have observed it in thick orange prisms, in long yellow needles, or in pointed crystals shaped like a spear-head.[1] It is slightly soluble in water and in alcohol. Water is the best solvent for it, good crystals being easily obtained from the aqueous solution.

Ferrocyanide, $(C_7H_7(CH_3)_2N)_2H_4Fe(CN)_6$.—This substance was obtained as a white precipitate, when a solution of potassic ferrocyanide was added to a slightly acid solution of the chloride. It contains no water of crystallisation, and its composition was determined by the following analyses :

I. 0.5224 gram of the salt dried in vacuo gave on ignition 0.0852 gram of ferric oxide.

II. 0.3714 gram gave 0.0612 gram of ferric oxide.

	Calculated for $[C_7H_7(CH_3)_2N]_2H_4Fe(CN)_6$.	I.	Found. II.
Iron	11.53	11.41	11.53

Properties.—It forms white, pearly scales, which are very sparingly soluble in water, and on exposure to the air turn slightly green, but the amount of the decomposition thus indicated is so small as to be inappreciable by analysis.

With mercuric chloride the base gave an uninviting, viscous product, while with zincic chloride it formed a characteristic double salt, which separated from concentrated solutions as an oil, but soon solidified in good-sized rhombic crystals ; an analysis of a not perfectly pure sample of this salt led to the following results :

0.3492 gram of the salt gave 0.4090 gram of argentic chloride.

	Calculated for $[C_7H_7(CH_3)_2NHCl]_2ZnCl_2$.	Found.
Chlorine	29.65	28.95

Dibenzyldimethylammonic Chloride, $(C_7H_7)_2(CH_3)_2NCl$.—This substance was left in the aqueous solution after the benzyldimethyl-

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[1] The identity of the substance in all these forms was proved by analyses.

amine had been shaken out with ether, and, when this solution was evaporated to one-half its original volume, separated as a yellow oil, which solidified as it cooled. It can be freed partially from the inorganic salts present mechanically, or by solution in chloroform, although chloroform does not remove it from its aqueous solution, and purified by washing with a saturated solution of sodic carbonate, and finally dissolving it out of the inorganic impurities with alcohol or chloroform.

Properties.—It forms white rhombic crystals, often in spear-head forms and a centimetre broad, or masses of radiating prisms or needles, but usually separates from its solutions as an oil, which solidifies after standing for some time, more rapidly if touched with a crystal of the substance. It is freely soluble in water, but nearly insoluble in a saturated solution of sodic carbonate, soluble with some difficulty in alcohol, but freely in chloroform, which is the best solvent for it; it is also soluble in ether, benzol, carbonic disulphide, and glacial acetic acid, insoluble in ligroine. When heated, it gives benzylchloride, recognised by its smell and its action on the eyes, and a base, which, however, seems to boil at a higher temperature than the benzyldimethylamine; but the experiment should be repeated on a larger scale. If the aqueous solution of the chloride is boiled with argentic oxide, it becomes strongly alkaline, but it is necessary to boil for some days in order to convert it completely into the free base.

Dibenzyldimethylammonic Chlorplatinate, $[(C_7H_7)_2(CH_3)_2N]_2$-$PtCl_6$.—This substance was prepared by adding an alcoholic solution of the chloride to chlorplatinic acid, and purified by recrystallising from water. Its composition was determined by the following analysis:

0.2012 gram of the salt gave 0.0454 gram of platinum.

	Calculated for $[(C_7H_7)_2(CH_3)_2N]_2PtCl_6$.	Found.
Platinum	22.64	22.56

It is nearly insoluble in cold water, but crystallises from a hot aqueous solution in large, shining, yellow plates often a centimetre in length, or in feather-like forms.

L.—A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF HYDROXYL.

BY C. LORING JACKSON AND G. W. ROLFE.

The methods now in use for determining the number of hydroxyl radicals in a molecule can be divided into two classes—those which consist in the analysis of the acetyl or benzoyl compound, and those which depend on the saponification of the acetyl compound and the quantitative determination of one or other of the products of the decomposition. Methods of the first class cannot be applied to substances having large molecular weights, as then the differences in percentage composition approach the limit of error of the analysis ; and even methods of the second sort have led to false conclusions in many cases (for instance, with æsculine and æsculetine, which give soluble compounds with magnesic hydrate), or are inapplicable, owing to the instability of the compound with saponifying agents. We have worked out, therefore, a new method for determining hydroxyl quantitatively, which is applicable in cases where the methods now in use can be applied only with difficulty or give uncertain results, and, we hope, will commend itself also in other cases on account of its simplicity, as it does away with the additional operation of saponification—often a tedious one—necessary in methods of the second class.

Our process consists in converting the substance into its parabrombenzoyl compound, and determining the amount of bromine introduced by an analysis according to the method of Carius. It therefore belongs with methods of the first class, but has the advantage that the differences in percentage composition are larger than when carbon and hydrogen are determined in the benzoyl or acetyl compounds, as is shown by the following comparison of the differences caused by the presence of one more hydroxyl in the molecule between the percentages of carbon in the benzoyl and of bromine in the brombenzoyl derivatives of æsculetine, æsculine, and fisetine,[1] substances which we have selected for calculation on account of the differences in their molecular weights.

Name and Formulas of Substance.	Benzoyl Compound. Difference in percentage of C.	Brombenzoyl Compound. Difference in percentage of Br.
Æsculetine, $C_9H_3O(OH)_3$ $C_9H_4O_2(OH)_2$	1.97	3.60

[1] Schmid, Berichte d. deutsch. chem. Gesell. **19**, 1351.

Æsculine, $\left.\begin{array}{l}C_{15}H_{10}O_3(OH)_6 \\ C_{15}H_{11}O_4(OH)_5\end{array}\right\}$	0.90	1.50
Fisetine, $\left.\begin{array}{l}C_{23}H_{10}O_3(OH)_6 \\ C_{23}H_{11}O_4(OH)_5\end{array}\right\}$	0.78	1.66

The numbers given in the third column of the above table are far enough removed from the maximum analytical error to leave no doubt in regard to the composition of the substance; and we may add that, as far as our experiments go, the parabrombenzoates show a much greater tendency to crystallisation than the corresponding benzoates, so that in most cases the error from incomplete purification can be reduced to a minimum.

In deciding which acid containing bromine was the best adapted to our purpose, we rejected the fat acids, although, other things being equal, they were to be preferred on account of the greater differences in the percentages of bromine, because we feared the removal of a portion of the bromine in the preparation or purification of the ester, and accordingly selected from the aromatic acids that one which we found could be prepared most easily—that is, the parabrombenzoic acid.

In the remainder of the paper we give the details of the methods which we found most convenient for the preparation of the parabrombenzoic acid and its chloride and anhydride, as well as a few experiments on the formation of parabrombenzoyl esters, undertaken to determine whether these bodies could be formed as easily as the corresponding benzoyl compounds; but we have not considered it necessary to extend these experiments to the less accessible substances, or to multiply them for the commoner bodies, as those which we have tried are sufficient to prove the general application of the method; showing that the parabrombenzoylchloride is as reactive as benzoylchloride, and that the anhydride, although, on account of its high melting-point, somewhat less manageable than the non-substituted one, acts excellently on all substances which can stand a high temperature, and can usually be made to act on those which cannot by heating with anhydrous benzol in a sealed tube. As all the derivatives of parabrombenzoic acid described in this paper, with the exception of the chloride, are new, we give a full account of their properties, as a contribution to our knowledge of this hitherto neglected acid.

Preparation of Parabrombenzoic Acid.

Although this method offers no new features, we think it best to
describe it as a matter of convenience for those who may wish to
obtain the acid in quantity. The first step is the preparation of
crude monobromtoluol by mixing toluol with ten per cent. of its
weight of iodine and the calculated amount of bromine. After the
mixture has stood at the ordinary temperature for twelve hours,
the product is washed with sodic hydrate and water, the bromtoluol
fractioned, and the portion boiling from 180° to 190° oxidised by
boiling 150 grams of it in a flask with a return-condenser for twelve
hours with 400 grams of potassic dichromate and 550 grams of
sulphuric acid diluted with twice its bulk of water. The unoxi-
dised oil, consisting of orthobromtoluol with a little para, is dis-
tilled off with steam, and the acid purified by washing with water
and conversion into the sodic salt. The product is free from the
isomeric brombenzoic acids, as shown by its melting-point, 248°–
250° (uncorr.). The yield varied from 40 to 70 per cent. of the
weight of crude bromtoluol used, and a preparation can be carried
through from toluol to the pure acid in less than one week.

Parabrombenzoylchloride, $C_6H_4BrCOCl$.—This substance has
been prepared by J. W. Raveill,[1] under the direction of Hübner;
but he gives only the most meagre description of it, stating that it
forms colorless, easily fusible, volatile needles. It is prepared
without difficulty by heating a mixture of phosphoric pentachloride
and the dry acid in a flask to 100° until the reaction has ceased,
when the temperature is to be raised to 150°, and kept at this point
until the greater part of the phosphoric oxychloride formed has
passed off. The chloride is then extracted with ligroine and
purified by distillation. The yield is about 80 per cent. Its com-
position was determined by the following analyses:

I. 0.4010 gram of the substance gave on combustion 0.5575
gram of carbonic dioxide and 0.0745 gram of water.

II. 0.2273 gram gave by the method of Carius 0.3448 gram of
the mixture of argentic chloride and bromide.

III. 0.4160 gram gave by the same method 0.6278 gram of the
mixture of argentic chloride and bromide.

IV. 0.3014 gram gave, when boiled with a solution of pure
potassic hydrate, after acidification with nitric acid and precipita-
tion with argentic nitrate, 0.1962 gram of argentic chloride.

[1] Annalen der Chemie **222**, 178, note.

V. 0.4284 gram gave by the same method 0.2773 gram of argentic chloride.

	Calculated for $C_6H_4BrCOCl$	I.	II.	Found. III.	IV.	V.
Carbon	38.26	37.92	...	...	...	...
Hydrogen	1.82	2.06	...	...	...	...
Chlorine and bromine	52.62	...	52.61	52.86	...	...
Chlorine	16.17	...	...	...	16.08	16.01

Properties.—White needles with an odor similar to that of benzoylchloride, but much less marked, owing to its higher boiling-point; melting-point, 30°. It boils at 245°–247°[1] (uncorr.) with slight decomposition; water does not dissolve it, and acts upon it very slowly, if at all, in the cold, more rapidly when boiling; it is easily soluble in ligroine or benzol, while alcohol dissolves it with conversion into the ethyl ester, a viscous liquid with an odor similar to that of oil of anise.

Parabrombenzoic Anhydride, $(C_6H_4BrCO)_2O$.—This substance was prepared by heating the sodic parabrombenzoate with para-brombenzoylchloride, not in excess; convenient proportions are 3 grams of the sodic salt to 2 grams of the chloride. The mixture was heated in a flask with an air-condenser for an hour to 200° by means of a paraffine bath, and the product purified by washing, first with ligroine, then with a strong solution of sodic carbonate, and finally with benzol to remove the tarry impurities. The yield was about 50 per cent. Owing to its very slight solubility in all the common solvents, we did not attempt to purify it by crystallisation, but this was fortunately unnecessary, as the following analyses show that the substance purified as above by washing is essentially pure:

I. 0.2310 gram of the substance gave by the method of Carius 0.2260 gram of argentic bromide.

II. 0.2167 gram gave 0.2138 gram of argentic bromide.

	Calculated for $(C_6H_4BrCO)_2O$	Found. I.	II.
Bromine	41.67	41.64	41.99

Properties.—As obtained by the method described above, it forms an odorless, bulky white powder; crystallised from chloroform, it forms minute oblong, rectangular plates; from benzol, small, pointed needles; melting-point, 212°–213°. It is insoluble in water, and

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[1] It was not thought worth while to try to determine this temperature with greater accuracy, because of the decomposition with which the boiling is accompanied.

apparently not decomposed by it even when boiling; almost insoluble in ether, glacial acetic acid, or carbonic disulphide; slightly soluble in benzol, somewhat more so in chloroform, which is the best solvent for it; hot alcohol dissolves it freely, converting it into the ethyl ester, as shown by the characteristic odor of that substance.   Cold sodic hydrate is essentially without action on it, but decomposes and dissolves it slowly when warmed with it.

Phenylparabrombenzoate, $C_6H_4BrCOOC_6H_5$.—This substance was made by heating phenol and parabrombenzoylchloride in a flask with a return-condenser to about 200°.   It was also prepared from phenol and parabrombenzoic anhydride at the same temperature.   The product, a waxy solid, was purified by crystallisation from alcohol, dried at 100°, and analysed.

I. 0.1927 gram of the substance gave by the method of Carius 0.1295 gram of argentic bromide.

II. 0.1051 gram gave 0.0710 gram of argentic bromide.

	Calculated for $C_6H_4BrCO_2C_6H_5$.	Found. I.	II.
Bromine	28.88	28.61	28.76

Properties.—White scales with a pearly lustre somewhat resembling naphthaline; it has a slight, agreeable odor, and melts at 117°.   It is insoluble in water, readily soluble in alcohol, methyl alcohol, ether, benzol, chloroform, or carbonic disulphide, less so in ligroine, and not freely soluble in glacial acetic acid.   Alcohol is the best solvent for it.

Phenylbenzoate is a well-crystallised substance melting at 68°–69°.

Pyrogallol Triparabrombenzoate, $(C_6H_4BrCOO)_3C_6H_3$.—This substance was made by the action of parabrombenzoylchloride on pyrogallol at 100° for six hours.   After removing the excess of the chloride with ligroine, the residue was washed with a boiling solution of sodic carbonate, and the slightly yellowish waxy solid purified by crystallisation from hot benzol.   Its composition was determined by the following analyses :

I. 0.1569 gram of the substance gave by the method of Carius 0.1322 gram of argentic bromide.

II. 0.1153 gram gave 0.0963 gram of argentic bromide.

	Calculated for $(C_7H_4BrO_2)_3C_6H_3$.	Found. I.	II.
Bromine	35.56	35.85	35.55

Properties.—It forms a white, crystalline powder made up of microscopic, diamond-shaped plates, which belong to the monoclinic

system, to judge from their behavior toward polarised light; melting-point, 140°. Freely soluble in benzol, ether, or chloroform, very slightly soluble in alcohol, glacial acetic acid, or carbonic disulphide, and essentially insoluble in water or ligroine. Hot benzol is the best solvent for it.

It is an important point in favor of our method that this is a crystalline substance, whereas the product of the action of benzoylchloride on pyrogallol was, according to Nachbaur,[1] resinous, and the difficulties in the way of its purification were so great that its formula could not be determined with certainty.

Parabrombenzamide,$C_6H_4BrCONH_2$.—This substance was prepared, as a contribution to our knowledge of the derivatives of parabrombenzoic acid, by the action of strong ammonic hydrate on the parabrombenzoylchloride. The white, curdy precipitate thus obtained was purified by three recrystallisations from boiling water. Its composition was determined by the following analyses:

I. 0.3012 gram of the substance gave 18.6 cc. of nitrogen gas under a pressure of 767 mm. and a temperature of 18°.

II. 0.1326 gram of the substance gave by the method of Carius 0.1260 gram of argentic bromide.

	Calculated for $C_6H_4BrCONH_2$.	Found. I.	II.
Nitrogen	7.00	7.20	...
Bromine	40.00	...	40.44

Properties.—It forms small white, rectangular plates with a pearly lustre; melting-point, 186°. It is insoluble, or nearly so, in cold water, soluble in hot, and in alcohol, ether, or glacial acetic acid, very slightly soluble in chloroform, and essentially insoluble in ligroine, benzol, or carbonic disulphide.

ON THE ACTION OF BROMINE ON ISOBUTYLENE.

By L. M. Norton and H. J. Williams.

During the preparation of a large quantity of isobutylene bromide by the absorption of isobutylene in a solution of bromine in carbon disulphide, we observed that the theoretical yield of iso-

[1] Wien. Acad. Ber. **24,** 270.

butylene bromide was not obtained. The isobutylene was prepared by the action of alcoholic soda solution on pure isobutyl iodide,[1] and was then absorbed in a series of bottles containing a mixture of equal volumes of bromine and carbon disulphide. The carbon disulphide and isobutylene bromide were removed by distillation, and a very considerable residue with a high boiling-point remained. By fractionation at a pressure of 235 mm., a liquid boiling at 173°–183° at that pressure was obtained from the residue just mentioned. This liquid possessed a yellow color, and analysis indicated that it was a tribrom-isobutane. Its specific gravity was 2.15 at 17° compared with water at the same temperature. The analysis gave:

	Found.	Calculated for Tribrom-isobutane.
Br	80.95	81.35
H	2.85	2.37
C	17.05	16.27

For further examination the tribrom-isobutane was treated with alcoholic soda solution in the proportion of one mol. of sodium hydrate to one mol. of tribrom-isobutane. The liquid obtained by the action of the soda, after freeing it from alcohol, was purified by fractionation and boiled constantly at 158°–161°. It possessed a yellow color. Two bromine estimations gave 51.59 per cent. and 51.48 per cent. of bromine, while the dibrom-isobutylene, which the treatment described above should have furnished, would contain 74.77 per cent. of bromine. The new compound did not absorb bromine, and was perhaps an isobutylene bromhydrine which would contain 52.28 per cent. of bromine.

It seemed desirable to compare our tribrom-isobutane with a tribrom-isobutane of known structure. For this purpose isocrotyl bromide[2] boiling at 91°–92°, prepared by the action of alcoholic soda solution on isobutylene bromide, was treated with bromine. The tribromide thus obtained was purified by fractionation under reduced pressure, and boiled constantly under a pressure of 235 mm. at 155°–161°. Its specific gravity at 17°, compared with water at the same temperature, was 2.187. An analysis gave:

	Found.	Calculated for Tribrom-isobutane.
Br	80.91	81.36

[1] Chapman and Smith, Jour. Chem. Soc. **7**, 153.   [2] Butlerow, Zeit. f. Chem. 1870, 523.

By treatment with alcoholic soda this tribrom-isobutane was converted into a dibrom-isobutylene which boiled constantly at 154°–155°, and is identical with that mentioned by Caventou,[1] and obtained by him from a butylene formed by the action of heat on fusel oil. By the action of bromine this dibrom-isobutylene was converted into a tetrabrom-isobutane which contained:

	Found.	Calculated for Tetrabrom-isobutane.
Br	85.54	85.56

This compound crystallises from ether in beautiful long plates. It is easily soluble in alcohol and ether. It melts with decomposition at 205°, and is without doubt identical with that obtained by Caventou in the above-mentioned research. It appears probable, therefore, that Caventou obtained isobutylene by the action of heat on fusel oil. Isobutylene was obtained in this way by Butlerow,[2] and the butylene of Wurtz,[3] also obtained in the same way and hitherto considered to be pseudobutylene, may perhaps have been isobutylene.

A comparison of the tribrom-isobutane formed by the action of bromine on isobutylene and that formed by the addition of bromine to isocrotyl bromide, leads us to believe that the two tribrom-isobutanes are not identical, since they differ, as the results given above show, in their physical properties and widely in their behavior toward alcoholic soda solution. According to the views ordinarily held, only two tribrom-isobutanes could be formed from isobutylene—viz. $(CH_3)_2 : CBr : CHBr_2$ and $CH_3 : CH_2Br : CBr : CH_2Br$. To the tribrom-isobutane formed from isocrotyl bromide the structure $(CH_3)_2 : CBr : CHBr_2$ must be assigned. There remains only the symbol $CH_3 : CH_2Br : CBr : CH_2Br$ for the tribrom-isobutane formed by the action of bromine on isobutylene. It is probable that the formation of tribrom-isobutane from isobutylene takes place simultaneously with the union of bromine with isobutylene, as we were unable to obtain any tribrom-isobutane by allowing isobutylene bromide to remain in contact with a solution of bromine in carbon disulphide for several weeks.

Massachusetts Institute of Technology, Boston.

[1] Ann. d. Chem. **127**, 96.   [2] Ann. d. Chem. **145**, 277.
[3] Ann. d. chim. et phys. [3], **55**, 452.

THE ACTION OF FERRIC SULPHATE ON IRON.

By Albert E. Menke.

The deleterious action of ferric sulphate on boilers has been the cause of much trouble to engineers, owing to the fact that it appears to cause rapid corrosion. Experiments have been made to determine the action of ferric sulphate in solutions of different strengths on different irons, and to see how far it is possible to stop the destructive effects. In the first series of experiments pure iron wire was taken, a certain amount of water and ferric sulphate added, and the whole then heated in flasks with reversed coolers. For purposes of comparison, blank experiments were made with iron and water, leaving out the ferric sulphate. The following results were obtained:

No. of Expt.	Actual Loss.	Calculated on Blank.	Rust Formed.	Amount $Fe(SO_4)_3$ Used.	Weight Fe Taken.
1	.0135	.0133	.0002	.0016	1.1515
2	.0115	.0111	.0004	.0032	.9590
3	.0130	.0112	.0018	.0048	.9660
4	.0193	.0128	.0065	.0064	1.0965
5	.0161	.0108	.0053	.0080	.9314
6	.0214	.0135	.0076	.0096	1.1720
7	.0198	.0122	.0076	.0144	1.0507
8	.0040	.0032	.0008	.0016	.2816
9	.0080	.0033	.0047	.0032	.2805
10	.0050	.0036	.0014	.0048	.3130
11	.0030	.0028	.0002	.0064	.2440
12	.0035	.0026	.0009	.0080	.2295
13	.0036	.0028	.0008	.0096	.2464
14	.0070	.0032	.0038	.0144	.2800
15	.0030	.0030	.0030	None.	.2584
16	.0029	.0029	.0029	None.	.2576

The results in Column 3 were obtained by calculation from Experiments 15 and 16. All were heated the same length of time— fifteen hours. It will be noticed that there is a slight increase of oxidation as the strength of the ferric sulphate increases. The next set of experiments was made with the substances enclosed in sealed tubes and heated to 110° C. for fifteen hours.

No. of Expt.	Amount Rust Formed.	Fe₂(SO₄)₃ Used.	Weight Iron Taken.
17	.0005	.0016	.6930
18	.0006	.0016	.7390
19	.0008	.0032	.7860
20	.0005	.0032	.7830
21	.0010	.0048	.8350
22	.0015	.0048	.7700
23	.0002	None.	.7900

It will be noticed here, again, that the rust increases with the ferric sulphate. In the next set of experiments, Nos. 24 and 25 had nothing but the iron and ferric sulphate solution, Nos. 26 and 27 had the calculated amount of sodic carbonate, Nos. 28 and 29 the potassic carbonate, and Nos. 30 and 31 the calcic carbonate requisite for decomposing the ferric sulphate. These experiments were made in sealed tubes heated to 110° C. for fifteen hours. The results are interesting, and show that the alkaline carbonates have a good effect in stopping the formation of rust.

No. of Expt.	Amount Rust Formed.	Fe₂(SO₄)₃ Used.	Weight Iron Taken.
24	.0025	.0093	.9596
25	.0028	.0093	.9331
26	.0010	.0093	.9318
27	.0011	.0093	.9166
28	.0010	.0093	.9504
29	.0006	.0093	.9431
30	.0023	.0093	1.0178
31	.0024	.0093	.9666

In the next set of experiments the temperature was raised to 160° C., the tubes being heated, however, only three hours.

No. of Experiment.	Rust Formed.	Fe₂(SO₄)₃ Used.	Weight Iron Taken.
32	.0012	.0934	.8898
33	.0004	.0934	.9192
34	.0006	.0934	.9564
35	.0005	.0934	.9340

The action here has been more rapid as the temperature and pressure increased. The next series of experiments was made with boiler-iron of good quality. The pieces of iron used were about one-half inch long, one-eighth inch thick and one-eighth inch wide. The action was not as vigorous as in the experiments with pure iron.

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No. of Expt.	Rust Formed.	Fe$_2$(SO$_4$)$_3$ Used.	Wt. Iron Taken.	Remarks.
36	.0101	.0934	7.2561	Alone.
37	.0089	.0934	8.6119	Alone.
38	.0045	.0934	9.1265	+ NaHCO$_3$
39	.0035	.0934	8.8775	+ NaHCO$_3$
40	.0040	.0934	9.6142	+ K$_2$CO$_3$
41	.0030	.0934	7.9619	+ K$_2$CO$_3$
42	.0046	.0934	8.9392	+ CaCO$_3$
43	.0046	.0934	7.5256	+ CaCO$_3$

The above experiments were conducted in sealed tubes heated to 110° C. for 15 hours.

The next set of experiments was made in sealed tubes heated to 160° C. for 3 hours.

No. of Experiment.	Amount Rust Formed.	Fe$_2$(SO$_4$)$_3$ Used.	Weight Iron Taken.	Remarks.
44	.0124	.0934	8.2238	Alone.
45	.0052	.0934	6.5678	+ NaHCO$_3$
46	.0048	.0934	6.5075	+ K$_2$CO$_3$
47	.0076	.0934	7.3948	+ CaCO$_3$

The action here, as when pure iron was used, has been more rapid. This was proven to be the case by making two experiments and testing the amount of rust formed every hour for ten hours successively. In the tube heated to 110° the action was gradual; in the tube heated to 160° most of the rust was formed in the first hour. How long the action goes on, and at what rate it progresses, has not yet been determined. The next set of experiments was made with small pieces of steel, and here the action was the slowest.

No. of Experiment.	Rust Formed.	Amount Fe$_2$(SO$_4$)$_3$ Used.	Wt. of Steel Taken.	Remarks.
48	.0064	.0934	7.7526	Alone.
49	.0062	.0934	7.6843	Alone.
50	.0020	.0934	7.4232	+ K$_2$CO$_3$
51	.0025	.0934	7.3965	+ K$_2$CO$_3$
52	.0031	.0934	7.5742	+ NaHCO$_3$
53	.0028	.0934	7.4962	+ NaHCO$_3$
54	.0048	.0934	7.7922	+ CaCO$_3$
55	.0042	.0934	7.7800	+ CaCO$_3$

The above were heated to 110° C. in sealed tubes.

The following were heated to 160° C. in sealed tubes:

No. of Expt.	Rust Formed.	Amt. Fe₂(SO₄)₃ Used.	Wt. of Steel Taken.	Remarks.
56	.0072	.0934	7.8423	Alone.
57	.0030	.0934	7.6364	$+ NaHCO_3$
58	.0026	.0934	7.7982	$+ K_2CO_3$
59	.0041	.0934	7.6541	$+ CaCO_3$

Potassium carbonate all through seems to be the best preventive, but its expense will, in most instances, preclude its use. Sodic carbonate was tried in all kinds of proportion, but in no case was there complete arrest of the oxidation. The best amount of sodic carbonate to use is 1½ grains for every grain of ferric sulphate found in the water. Further experiments in the retarding of rust-formation are now in progress.

KENTUCKY STATE COLLEGE.

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ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.

IV.

BY W. A. NOYES AND CHARLES WALKER.

In the last paper[1] it was shown that ortho-toluene sulphamide when oxidised with potassium ferricyanide gives ortho-sulphamine-benzoic acid. As similar substances which have been oxidised by other agents have yielded sulphinides instead of ortho-sulphamine acids, it was of interest to determine whether other ortho sulphamides would conduct themselves in the same way as ortho-toluene sulphamide toward potassium ferricyanide.

The substance chosen for the investigation was para-xylene sulphamide. The para-xylene used was obtained from Kahlbaum. In cold weather it solidified, and the portion which became liquid at 12.5° was drained from the crystals. From the latter the amide was prepared in the usual way. It fused at 147°–148° (uncorr.).

Oxidation of Para-xylene Sulphamide.

The oxidation was effected with somewhat larger quantities than have been used in previous experiments. A mixture of 10 grams

[1] This Journal **8**, 176.

of the amide, 250 grams of potassium ferricyanide, 100 grams of caustic potash and 1000 cc. of water was boiled for about five hours. The oxide of iron which separated was filtered off, the filtrate was cooled, and enough dilute sulphuric acid was added to cause a slight evolution of carbon dioxide. This precipitated most of the unoxidised amide, which was then filtered off and used for a second oxidation, conducted in the same manner as the first. The solutions obtained from the two oxidations were evaporated and the potassium ferrocyanide was mostly removed by crystallisation. The solution was then acidified with sulphuric acid and extracted with ether. The impure acid which remained on distilling the ether was converted into the barium salt, and the solution of the latter was evaporated to dryness and the residue was treated several times with strong alcohol. This dissolved the unoxidised amide which it contained and also, as will be seen further on, a small quantity of a barium salt. The salt which remained was found to consist mainly of *barium sulphamine terephthalate*, which was easily obtained pure by dissolving the salt in a considerable amount of hot water and evaporating the solution till the salt separated.

Sulphamine-terephthalic Acid.

Considerable difficulty was experienced at first in obtaining the free acid in a state of purity, owing to the slight solubility of its barium salt, and to the fact that, when the salt is heated with hydrochloric acid, it is rapidly converted into mono-hydro-barium sulpho-terephthalate. It was shown by a special experiment that by evaporating a few times with hydrochloric acid, the conversion is almost quantitative, the amido group being split off and forming ammonium chloride. The barium salt obtained contained no nitrogen.

0.1385 gram of the salt lost 0.0063 gram H_2O at 260° and gave 0.0811 gram $BaSO_4$, which correspond to 4.55 per cent. H_2O and 34.43 per cent. Ba. Theory requires for $C_6H_3-SO_3\!\!\begin{array}{c}\diagup CO_2\\ \diagdown CO_2H\end{array}\!\!> Ba$ + H_2O, 4.51 per cent. H_2O and 34.34 per cent. Ba. The acid itself is decomposed in a similar way, though less easily, by evaporating with hydrochloric acid.

The acid was finally obtained by adding to the barium salt somewhat more than enough dilute hydrochloric acid to decom-

pose it and extracting with ether in a large test-tube. On distilling the ether and crystallising from hot water, the acid was easily obtained pure. *Sulphamine-terephthalic acid* is difficultly soluble in cold water, ether, or alcohol. It is easily soluble in hot water, and crystallises from the solution, on cooling, in fine needles concentrically grouped. The acid may be heated to 170° without loss in weight. It loses weight slowly at 220°, but no good evidence could be obtained that it was converted into the corresponding sulphinide. The best evidence that it is not converted into the sulphinide, however, lies in the fact that the acid does not fuse at 310° (corr.), while the sulphinide fuses at 297°–299° (corr.). The acid fuses with decomposition over the free flame.

I. 0.1064 gram of the acid gave 0.1033 gram BaSO₄ (Keiser).

II. 0.1046 gram of the acid gave 0.1000 gram BaSO₄ (Carius).

III. 0.1101 gram of the acid gave 0.00625 gram N.

	Calculated for $C_6H_3-SO_2NH_2$ $\diagup$ COOH $\diagdown$ COOH	I.	II.	III.
			Found.	
S	13.06	13.32	13.15	...
N	5.71	...	...	5.68

Mono-potassium Sulphamine Terephthalate,

$C_6H_3-SO_2NH_2 \diagup CO_2K \diagdown CO_2H + \frac{1}{2}H_2O$. This was prepared by adding to a weighed amount of the acid the calculated amount of a standard solution of potassium carbonate and evaporating the solution slightly. On cooling, the salt separated in needles radiating from centres and forming half-balls on the sides of the beaker. The acid potassium salt of terephthalic sulphinide was prepared, for comparison, exactly as described by Remsen and Hall,[1] and it showed no similar tendency. The salt is difficultly soluble in cold water. It loses nothing in weight at 150°–170°. At 200°–210° it loses weight slowly. At 250°, or a little above, it seems to decompose slightly, as in the first three analyses, in which the salt was heated till the weight was constant at that temperature, the loss was respectively 4.07, 4.18 and 4.28 per cent., which would correspond very closely to two-thirds of a molecule of water. The salt was turned slightly brown in each case, however; and as the salt in the third analysis lost only 3.37 per cent. on the first heating, at

[1] This Journal **2**, 58.

245°, while that of the fourth analysis lost only 2.90 per cent. on heating for three and one-half hours at 240°–245°, it seems probable that the salt really contains only one-half of a molecule of water.

I. 0.1204 gram lost 0.0049 gram H_2O at 250° and gave 0.0352 gram K_2SO_4.

II. 0.1003 gram lost 0.0042 gram H_2O at 250° and gave 0.0296 gram K_2SO_4.

III. 0.1633 gram lost 0.0055 gram H_2O at 245° and gave 0.0479 gram K_2SO_4.

IV. 0.0345 gram lost 0.0010 gram H_2O at 240°–245° and gave 0.01015 gram K_2SO_4.

	Calculated for $C_6H_3{-}{\overset{\diagup CO_2K}{\underset{\diagdown CO_2H}{SO_2NH_2}}}+ \frac{1}{2}H_2O$.		Found.		
		I.	II.	III.	IV.
$\frac{1}{2}H_2O$	3.08	4.07	4.18	3.37	2.90
K	13.35	13.11	13.23	13.15	13.19

Barium Sulphamine Terephthalate,

$C_6H_3{-}{\overset{\diagup CO_2}{\underset{\diagdown CO_2}{SO_2NH_2}}}{>}Ba + H_2O.$ When the impure sulphamine-terephthalic acid first obtained by evaporating the ethereal extract is boiled with water and barium carbonate, the barium salt which is formed goes into solution easily and remains dissolved in a comparatively small amount of water. If, however, the salt is once separated from the solution by evaporation, the salt which is deposited becomes very difficultly soluble and requires a large amount of hot water to bring it into solution again. The salt is deposited, on cooling its hot solution, in warty masses without any well-defined crystalline structure. Salts of different preparations, after drying over calcium chloride, lost at 210°–220° amounts of water varying from one to two molecules. The determinations of water given were made with the salt which gave the best evidence of being homogeneous in structure.

I. 0.2859 gram of the salt dried over $CaCl_2$ lost 0.0132 gram H_2O at 220°.

II. 0.3357 gram of the salt dried over $CaCl_2$ lost 0.0157 gram H_2O at 220°.

	Calculated for $C_6H_3{-}{\overset{\diagup CO_2}{\underset{\diagdown CO_2}{SO_2NH_2}}}{>}Ba + H_2O.$	Found.	
		I.	II.
H_2O	4.52	4.62	4.68

I. 0.1141 gram of the anhydrous salt gave 0.0703 gram $BaSO_4$.

II. 0.1569 gram of the anhydrous salt gave 0.0961 gram $BaSO_4$.

III. 0.1880 gram of the anhydrous salt gave 0.00693 gram N.

	Calculated for C_6H_3—SO_2NH_2>Ba, $\diagup CO_2$ $\diagdown CO_2$		Found.	
		I.	II.	III.
N	3.68	...	...	3.68
Ba	36.05	36.23	36.01	...

Terephthalic Sulphinide.

Remsen and Hall,[1] in their study of terephthalic sulphinide, did not prepare the free sulphinide, but only its acid potassium salt. In order to establish more fully the difference between the sulphinide and sulphamine-terephthalic acid, it seemed of interest to prepare the former and also its barium salt. The acid potassium salt of terephthalic sulphinide was prepared exactly as described by Remsen and Hall. In order to prepare the free sulphinide in a similar case, Remsen and Stokes[2] decomposed an acid silver salt with hydrochloric acid. In the present instance it was found simpler to add dilute sulphuric acid (1 : 5 by volume) to the acid potassium salt and extract with ether in a large test-tube. On evaporating the ethereal solution and crystallising the residue from hot water, the sulphinide was easily obtained pure. It crystallises in short, thin prisms. It is moderately soluble in cold, easily in hot water, difficultly soluble in ether. It fuses at 297°–299° (corr.). One of the most characteristic differences between sulphamine-terephthalic acid and terephthalic sulphinide is that solutions of the latter give a precipitate with silver nitrate which is almost insoluble in dilute nitric acid. Sulphamine-terephthalic acid gives no similar precipitate. The analyses were as follows :

I. 0.1040 gram gave 0.1075 gram $BaSO_4$.

II. 0.0849 gram gave 0.0869 gram $BaSO_4$.

III. 0.0547 gram gave 0.00343 gram N.

	Calculated for C_6H_3—SO_2>NH. $\diagup CO$ $\diagdown CO_2H$		Found.	
		I.	II.	III.
N	6.17	...	...	6.27
S	14.10	14.20	14.05	...

[1] *Loc. cit.* [2] This Journal **6**, 268.

Barium Anhydro-sulphamine Terephthalate,

$$C_6H_3{-}SO_2{\overset{\diagup CO}{\underset{\diagdown CO_2}{>}}}N{>}Ba + 3H_2O.$$ This was obtained by boiling a
solution of the sulphinide with barium carbonate.   On evaporating
the solution on the water-bath, the salt was deposited in scales
which are very difficultly soluble in water.

I. 0.1532 gram lost 0.0197 gram H_2O at 250° and gave 0.0860
gram $BaSO_4$.

II. 0.1875 gram lost 0.0241 gram H_2O at 250° and gave 0.1048
gram $BaSO_4$.

	Calculated for $C_6H_3{-}SO_2{\overset{\diagup CO}{\underset{\diagdown CO_2}{>}}}N{>}Ba + 3H_2O.$	Found.	
		I.	II.
$3H_2O$	12.98	12.86	12.85
Ba	32.93	33.00	32.86

Formation of Sulphamine-para-toluic Acids.

While sulphamine-terephthalic acid is formed in larger quantity
than anything else when para-xylene sulphamide is oxidised by
means of potassium ferricyanide, it is not the only product of the
oxidation.   In recrystallising the barium salt which had been
purified by treatment with alcohol, after removing most of the
barium sulphamine terephthalate there remained in solution a
much more soluble barium salt.   Dilute hydrochloric acid pre-
cipitated an acid from this solution which, after several crystallisa-
tions from water, proved to be the same sulphamine-para-toluic
acid which was obtained by Remsen and Hall[1] by oxidising para-
xylene sulphamide with chromic acid.   These authors state that
the acid is insoluble in ether, while we obtained it from the ethereal
extract, and found that it was in reality slightly soluble in ether.
In other respects the acid obtained by us as described above
agreed in properties with those ascribed to sulphamine-para-toluic
acid.   It fused at 267° (uncorr.).   Fused with caustic potash in the
manner described by Remsen and Hall,[2] it yielded oxy-toluic acid,

$C_6H_3{\underset{\diagdown CH_3}{\overset{\diagup COOH}{-}OH}}\begin{smallmatrix}1,\\3,\\4,\end{smallmatrix}$ which fused at 206°–208°, and oxy-terephthalic
acid which did not fuse at 300°.   The acid was also analysed:
0.0981 gram gave 0.1064 gram $BaSO_4$, which corresponds to 14.89
per cent. of S.   Theory requires 14.79 per cent.

[1] This Journal **2**, 50.   [2] This Journal **2**, 54.

In the first part of this paper it was stated that the alcoholic solution obtained in the purification of the barium salts also contained a small quantity of a barium salt. The solution was evaporated to dryness and the residue was dissolved in a little hot water. On cooling the solution, most of the para-xylene sulphamide which it contained separated. This was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in hot alcohol, in which it was quite easily soluble. After cooling, an equal volume of ether was added. This caused the precipitation of the barium salt. After filtering, the residue was treated again in the same way, to remove the last traces of the para-xylene sulphamide. An attempt to crystallise the barium salt from water being unsuccessful, the aqueous solution was precipitated with hydrochloric acid. The acid separated as an oily liquid at first, but it soon solidified. Repeated crystallisation from hot water failed to give any pure substance from this. Different specimens fused at temperatures ranging from 190°–240°. The portion most easily soluble in hot water, which melted partially at 192°–193°, was fused with caustic potash. The fusion was dissolved in water and the solution was acidified with hydrochloric acid. On distilling the solution the distillate deposited a small amount of an acid which fused at 173°–174° (corr.), and whose solution gave a strong violet color with ferric chloride. This was evidently nearly pure

β-oxy-para-toluic acid, $C_6H_3\begin{smallmatrix}\diagup COOH & 1. \\ -OH & 2. \\ \diagdown CH_3 & 4.\end{smallmatrix}$ It must have come

either from para-toluic sulphinide or from a β-sulphamine-para-toluic acid containing the sulphamine group ortho to the carboxyl. The latter supposition seems the more probable.

The formation of a second sulphamine-para-toluic acid is of especial interest, as it shows that in this case, where there are two methyl groups to be oxidised, they are attacked with about equal ease by potassium ferricyanide, although one group is ortho and the other is meta to the sulphamine group.

ANALYSIS OF MILK.

By F. G. Short.

In carrying on a series of feeding experiments at this station, it
was found necessary to shorten and simplify as much as possible
the method of milk analysis. The experience of four years and
the analysis of over one thousand samples of milk have shown
that the following method is entirely satisfactory when the number
of samples is large and time and labor are important consider-
ations.

The following apparatus is required :

Hofmeister capsules of very thin glass, of a capacity of 10–15 cc.
Asbestos, of the long, silky variety, prepared by heating to redness
for one hour and kept in a glass-stoppered bottle. A five cc.
pipette graduated in tenths. Some form of continuous fat extractor.
Flasks holding about 100 cc. Dry ether, prepared by allowing
commercial stronger ether to stand over fused calcium chloride for
several days, with occasional shaking, and then distilling off.
Cheese-cloth that has been prepared by being extracted with dry
ether.

The milk is thoroughly mixed by pouring several times from
one vessel to another. A Hofmeister capsule about three-fourths
filled with the prepared asbestos is placed on the balance pan,
covered with a small beaker, and weighed. A small beaker weigh-
ing about twelve grams is kept in the balance for this purpose.

Two cubic centimetres of milk are allowed to run into the cap-
sule from the five cc. pipette ; the capsule is immediately trans-
ferred to the balance, covered with the beaker, and a second
weight taken. In a rich milk, such as was given by the Jersey
cows used in the experiments, it is impossible to measure the milk
with sufficient accuracy by means of a pipette. If the sample is
thoroughly mixed, two grams will be found sufficient for accurate
work. Enough asbestos must be used to entirely absorb the milk,
thus presenting a large surface for evaporation.

The capsules and contents are dried at 110° C. in a double-
walled oven containing a solution of chloride of calcium boiling

at 110° C. To the oven is attached an upright condenser, to return the steam from the boiling calcium chloride solution. The chloride of calcium bath is found preferable to an oven heated directly by gas, on account of the ease with which a constant temperature is maintained. The oven in the station laboratory has been in use for several months, and has not varied a degree centigrade in that time. The only precaution is that the solution must boil freely at 110° C. The capsules containing milk are allowed to remain in the oven two hours. For the first twenty minutes the door of the oven is left partly open, to allow the excess of water to pass off. The door is then closed, and a slow current of dry carbonic acid gas is passed through the oven. At the end of two hours the capsules are removed to a desiccator, cooled and weighed.

For the fat, an extractor of the form given by S. W. Johnson is used.[1] The capsule is wrapped in a piece of prepared cheesecloth, crushed between the fingers and slipped into the inside tube. The cloth should be packed tight, so that during the extraction the column of ether will nearly fill the inside tube. A dry, weighed flask is attached to the extractor, fifty cc. of dry ether are poured in, and the whole connected to an upright condenser. In the station laboratory twelve condensers are used, fixed in a wooden frame. The water enters at one side and passes successively through each condenser. The flasks dip into a copper tank, four inches square and two feet five inches long, containing water heated by a Bunsen burner. The apparatus, once adjusted, requires no further attention. At the end of two hours the flasks are removed and the ether distilled off. The flasks are then wiped dry and placed in the drying-oven, where they are heated three hours in an atmosphere of carbonic acid gas, cooled and weighed. A series of analyses of the same milk gave the following:

Solids.	Fat.
13.71	3.75
13.41	3.72
13.48	3.73
13.46	3.77
13.53	3.89
13.48	3.90
13.19	3.75

[1] American Journal of Science, June, 1877.

	13.30	3.73
	13.20	3.78
	13.26	3.82
	13.43	...
Average,	13.35	3.78 Average.
Highest,	13.71	3.72 Lowest.
Lowest,	13.19	3.90 Highest.

A comparison of the above method with that of Adams' gave the following:

	Fat by Adams's Method.	Fat by Station Method.
1	5.89	5.94
2	5.91	5.84
3	5.92	5.83
	Average, 5.89	5.87

The above method is also applicable to butter analysis. The sample of butter is prepared by the method given by S. M. Babcock.[2] The sample, of one-half to one pound, is placed in a wide-mouthed fruit jar, the cover screwed down, and the butter melted by immersing the jar in warm water. As soon as the sample is thoroughly melted, the jar is shaken vigorously until a perfect emulsion of water and fat is secured.

The shaking is continued until the butter is so nearly solid that no separation of water and fat can take place. To hasten the cooling the bottle is held under the water-faucet. A small (*oo*) porcelain dish is taken, two to four grams of prepared asbestos placed in it, and the whole weighed. Between two and three grams of butter are placed on the asbestos, and dish and contents weighed again. If enough asbestos is taken, the butter is all absorbed when heated, and no difficulty is found in transferring the dried fat to the extractor.

The butter is dried two hours at 110° C. in an atmosphere of carbonic acid gas, cooled and weighed. The dry fat is transferred to the extractor by means of a piece of cheese-cloth, and the dish washed out with a few drops of ether. Fifty cc. of ether are added and the extraction continued for one hour, as for milk.

A series of determinations on the same sample of butter gave:

[1] Analyst **10**, 50.   [2] N. Y. Agl. Station Report, 1836, 334.

Water.	Fat.
12.70	83.62
12.57	83.49
12.63	83.62
12.72	83.46
12.64	83.21
12.72	83.57
12.73	82.96
12.64	83.43
12.72	83.29
12.68	83.31
12.61	83.33

Average, 12.67   83.55 Average.
Highest, 12.73   83.62 Highest.
Lowest, 12.57   82.96 Lowest.

AGRICULTURAL EXPERIMENT STATION, MADISON, WIS., *March* 23, 1887.

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ON THE COMPOSITION OF POTATOES.

BY M. A. SCOVELL, DIRECTOR, AND ALBERT E. MENKE, OF THE KY. AGR. EXP. STATION.

The percentage of starch in potatoes has been considered to be in direct ratio with their specific gravity. There are several tables in existence; one by Heideprinn,[1] another by Marke,[2] have usually been adopted for their accuracy. We have made a great many determinations of starch in potatoes, and do not find that the tables agree with our results to a striking degree; nor, on the other hand, do the tables agree with each other: they have apparently been mostly calculated from a few determinations. We show in the table appended the discrepancies between our results and those heretofore accepted. The starch was determined by acting upon the dried and finely pulverised potato with sulphuric acid, and heating in closed bottles at a temperature of 110° C. for four hours, in order to insure conversion, and then titrating in the usual way

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[1] Landw. Versuch-station **20**, 17.   [2] Dingl. Polyt. Jour. **225**, 517.

with Fehling solution. In order to correct any error that might
ensue from the presence of sugar in the potato prior to the above
treatment, we squeezed out the juice from a corresponding sample
of undried potato, boiled it with acid as before, neutralised with
potash, decolorised with subacetate of lead, filtered, diluted, and
titrated with Fehling solution. This gave us the amount of sugar
and convertible substances present, which could then be deducted
by simple calculation from the amount found in the dried potato,
giving us the actual sugar due to starch. Our experiments were
made on various kinds of potatoes, with the following results:

VARIETY.	Specific Gravity	Dry Substance, Per Cent.	Per Cent. Dry Substance from Specific Gravity	Starch Per Cent.	Per Cent. Starch by Specific Gravity.	Per Cent. Sugar, Gum, etc., calculated as Glucose.	Specific Gravity of Juice.
Empire State	1.0902	22.40	23.98	15.48	16.35	0.88	1.0260
Early Rose, A.........	1.0902	22.08	23.98	15.15	16.35	0.99	1.0285
" B.........	1.0895	22.25	23.98	15.18	16.35	1.06	1.0275
" C.........	1.0861	21.72	23.02	14.57	15.42	0.97	1.0265
Triumph.............	1.0852	21.80	22.78	15.09	15.19	0.76	1.0245
Burbank, Castle.....	1.0923	21.46	24.46	14.98	16.81	0.74	1.0255
Beauty of Hebron....... ..	1.0849	21.29	22.78	14.56	15.19	0.94	1.0260
Early Ohio......	1.0828	21.10	22.30	14.35	14.73	0.77	1.0270
Jumbo........	1.0780	20.43	21.13	14.20	13.58	0.84	1.0245
Charter Oak......	1.0879	22.91	23.50	15.33	15.88	1.49	1.0310
Clark's No. 1	1.0919	22.35	23.98	15.29	16.35	1.06	1.0275
Perfect Peachblow	1.0843	22.22	22.54	15.12	14.96	1.32	1.0290
Pearl of Savoy............	1.0867	21.86	23.26	15.07	15.65	1.06	1.0275
St. Patrick......	1.0801	20.20	21.60	14.29	14.04	0.74	1.0240
White Star.	1.0878	21.82	23.50	15.11	15.88	0.81	1.0270
Shaker Russet.....	1.0731	20.42	19.95	13.91	12.44	0.84	1.0280
Dakota Red.........	1.0733	19 21	19.95	12.05	12.45	1.10	1.0280
Vanguard...	1.0828	21.03	22.37	14.76	14.73	0.87	1.0255
Burbank, B. D. P...........	1.0890	21.94	23.74	16.05	16.12	...	...
Burbank, A. & M	1.0700	20.45	21.37	14.59	13.81	...	...

We have endeavored to found a table on our results, but find
that varying conditions affect the percentage of starch in so
marked a degree, without producing a corresponding variation in
the specific gravity, that we cannot draw up any rigorous table.
An approximation to the per cent. of starch present is the best
that can be said of specific-gravity indications when different
varieties of potatoes are used. The per cent. of sugar in the
potato is also at considerable divergence from what might have
been expected from a mere specific-gravity determination.

In order to try the effect of various fertilisers on the per cent. of starch present, we made a series of experiments with Burbank potatoes. The per cent. of sugar seemed to keep in fairly constant ratio with the starch, but, as before, the specific gravity did not show the per cent. of starch. The experiments are tabulated below. One-tenth of an acre of ground was used in each experiment.

Variety.	Specific Gravity.	Dry Substance, Per Cent.	Dry Substance, Per Cent. from Sp. Gr.	Starch, Per Cent.	Starch, Per Cent. by Specific Gravity.	Per Cent. Sugar, Gum, etc., calculated as Glucose.	Specific Gravity of Juice.	Fertilisers.
Burbank.	1.0877	22.49	23.50	15.44	15.88	1.03	1.0260	None; potatoes small.
"	1.0843	21.31	22.54	15.34	14.96	0.63	1.0240	None; potatoes cut to 1 eye.
"	1.0741	20.60	20.18	14.80	12.67	0.76	1.0240	None; potatoes large, whole.
"	1.0827	21.50	22.30	15.28	14.73	0.68	1.0235	$NaNO_3$, 30 lbs.; K_2SO_4, 20 lbs.; Superphos., 60 lbs.
"	1.0748	21.04	20.41	15.20	12.89	0.75	1.0255	Superphos., 60 lbs.; $NaNO_3$, 30 lbs.; KCl, 20 lbs.
"	1.0794	21.75	21.36	15.97	13.81	0.95	1.0270	Superphos., 60 lbs.; K_2SO_4, 20 lbs.
"	1.0868	21.60	23.26	15.13	15.65	0.65	1.0240	Superphos., 60 lbs.; $NaNO_3$, 30 lbs.
"	1.0877	22.38	23.50	15.80	15.88	0.93	1.0260	$NaNO_3$, 30 lbs.; K_2SO_4, 20 lbs.
"	1.0882	22.15	23.50	15.56	15.88	0.74	1.0261	Mapes' fertiliser.
"	1.0918	22.74	24.46	15.98	16.81	0.88	1.0275	Blank.
"	1.0837	21.33	22.54	14.65	14.96	0.88	1.0275	Stable manure, 300 lbs.
"	1.0898	21.58	23.74	14.69	16.27	0.92	1.0270	Pulverised limestone, 100 lbs.
"	1.0880	21.85	23.50	15.43	15.88	0.96	1.0280	Homestead fertiliser, 60 lbs.

The nitrogenous constituents of potatoes are at present but partially investigated. They are with difficulty separable, and easily decomposed. We have made extractions by diffusion, and determined the amount of albuminoids in each successive extract. It would appear that a dilute solution of hydrochloric acid will extract seventy-five per cent. of the albuminoids present in potatoes. Three ounces of potatoes were cut up in very thin slices, and successively treated with water, dilute sodium chloride solution, dilute hydrochloric acid, boiling alcohol, dilute hydrochloric acid at 60° C., and cold dilute sodium carbonate. The thin slices were treated with water at the ordinary temperature for two days. The extract was brownish-red in color, and had a distinctive odor. This extract was now boiled down considerably,

when a coagulum separated out. The coagulum was filtered off, and the filtrate evaporated to dryness in a dish which contained sand; otherwise it was impossible to remove the residue from the dish. This process was adopted for each extract, and the albuminoids present were determined by burning with slaked lime. The odd numbers are the coagulums, and the even numbers the filtrates.

Number.	Per Cent. Albuminoids.	How Obtained.
1	.049625 }	H_2O, 2 days.
2	.047500 }	
3	.0033500 }	H_2O, 2 days.
4	.0312500 }	
5	.008700 }	.1 per cent. NaCl, 2 days.
6	.017500 }	
7	.039370 }	.1 per cent. HCl, 3 hours.
8	.103120 }	
9	.030620 }	.1 per cent. HCl, 2 days.
10	.455687 }	
11	.017500 }	C_2H_5OH, 5 hours.
12	.153120 }	
13	.019790 }	.1 per cent. HCl at 60° C., 6 hours.
14	.250937 }	
16	.050310	.2 per cent. Na_2CO_3, 2 days.
18	.313656	Residue dried and burnt.

The peptones present in Early Rose, Burbank, Charter Oak and Dakota Red potatoes were determined as follows: The potatoes were mashed in a crusher, the juice obtained was filtered, the filtrate acidified with acetic acid and boiled; the coagulum resulting was then filtered out. The filtrate was now partially decolorised with subacetate of lead, taking care to avoid any excess, the precipitate was filtered off and sulphuretted hydrogen passed through the solution to get rid of any excess of lead, again filtered, acidified with sulphuric acid, and phospho-tungstic acid was added to precipitate the peptones. The precipitate, after washing with acidulated water, was decomposed by baryta water; the yellowish filtrate containing the peptones was treated with carbonic anhydride, which precipitated the rest of the coloring-matter along with the barium carbonate. The quantity of peptone in solution was now estimated by making use of the biuret reaction and a standard solution of fibrin peptone. Again the peptones were precipitated by tannic acid, after precipitation of the albumen

by acetate of lead. The quantity of peptone obtained in this way differed from the amount obtained in the prior method. This was evidently to be accounted for by the fact that phospho-tungstic acid precipitates other matters besides peptones. In order to obtain the amount of peptones as accurately as possible, it is advisable to precipitate them fractionally. The first flocculent precipitate obtained contains all the peptones; the latter pulverulent precipitate contains none.

Variety.	Peptones.	Total Albuminoids.
Early Rose,	.0380 per cent.	2.19 per cent.
Burbank,	.0312	2.25
Charter Oak,	.0294	2.69
Dakota Red,	.0418	2.44

We expected that the Dakota Red potato would yield a much larger percentage of peptones than any other variety, owing to the large amount of solid matter other than starch contained in this potato. The excess of its peptone percentage is, however, but small.

The leucine and tyrosine were determined in the alcoholic extract of the dried potatoes and separated by fractional crystallisation. On concentration crystalline tufts of tyrosine were first deposited, and from the mother liquors, on further concentration, scales of leucine separated. The leucine melts at 170° C., and may be sublimed unchanged, is fairly soluble in water and but slightly so in absolute alcohol. The crude crystals of tyrosine may be purified by solution in hydrochloric acid and precipitation with sodium acetate, digestion with animal charcoal, if necessary, being previously resorted to with the acid solution. It forms long, silky crystals, very sparingly soluble in cold water and alcohol. We found the following amounts present in four varieties:

Early Rose,	.0074
Burbank,	.0068
Dakota Red,	.0092
Charter Oak,	.0070

Asparagin may be separated by adding alcohol to the potato juice and purifying the precipitate. We did not make any determinations of the amount present.

8

A METHOD FOR THE DETERMINATION OF BUTTER IN MILK.

BY H. N. MORSE AND C. PIGGOT.

Briefly stated, the method of which we here give a preliminary account consists in the dehydration of the milk by means of anhydrous sulphate of copper ; the extraction of the fat by means of the low-boiling products of petroleum ; the saponification of the butter by means of an excess of a standard solution of potassium hydroxide in alcohol ; and the determination of the excess of the alkali by means of a standard solution of hydrochloric acid.

The required apparatus and materials are :

1. A porcelain mortar, with lip, having an internal diameter of 85 or 90 millimetres.

2. An extraction tube, *A* in the figure, having an internal diameter of 14 or 15 millimetres, a length of 220 millimetres and a funnel end 75 millimetres wide.   The small end should be beveled. If such a tube is not at hand, a straight chloride of calcium tube of like dimensions and a copper funnel such as is usually employed in filling combustion tubes will suffice.   The narrow portion of the tube is filled with cleansed cotton wool, which should be compact enough to prevent the passage of solid matter, and yet not so tightly packed as seriously to impede the filtration of the fat solution.   One soon learns, by simply drawing air through the tube with the mouth, to judge correctly whether the filter will satisfy these conditions.

3. A 200 cc. Erlenmeyer flask, *B* in the figure, the strength of which should be tested by the filter pump before using.

4. A suitable stand to hold the flask and extraction tube in position.   The figure represents a very convenient form for the purpose.   A filter pump which will raise a column of mercury to a height of 26 inches suffices for the operation of five such apparatuses at the same time ; hence, for the sake of compactness and convenience, we employ them in series of five each, the bases being fastened together by screwing them down to a board placed underneath.   A half-inch brass tube with a small side tube for each flask is fastened to the base between the flasks and the standards.   Each side tube is attached to its flask by means of a

short piece of rubber tubing, and supplied with a Mohr's pinch-cock. One end of the larger tube is closed by a stopper, and the other attached to the filter pump.

5. A supply of 10 cc. full pipettes with but one mark. These should be tested, and only those selected which deliver very nearly the normal amount of water. If care is taken to use a clean pipette for each measurement, and to blow out all of the milk which can be removed from it, it is not necessary in ordinary work to weigh, since the difference between the weight of the milk calculated from the volume and the specific gravity, and that found by actual weighing, will only slightly affect the estimated percentage of butter in the second decimal place. We have convinced ourselves by repeated experiments that such wide differences between the estimated and determined weights of milk as are sometimes recorded are not necessary.
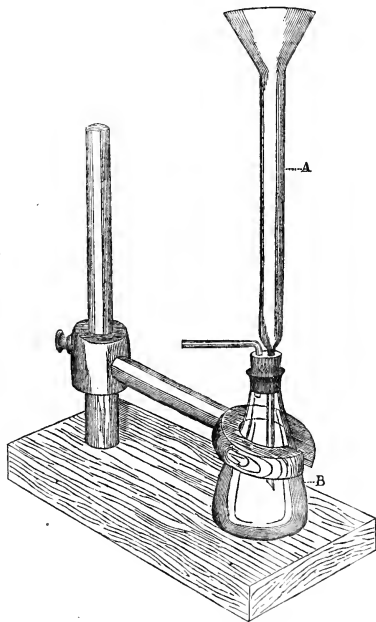
6. A number of small weighing glasses, with ground-glass stoppers, to be used when great accuracy in the deter-mination of the butter is required. These should be numbered, and the number of each written upon both the glass and its stopper.

7. A low-boiling "gasoline." This we are accustomed to pre-pare from the crude product known as "90° gasoline" by agitating it successively with strong sulphuric acid and sodium hydroxide and then distilling. Thus far we have employed only that portion

which distils over between 30° and 60°, though during the summer months it would probably be advisable to reject all of that which comes over below 40° or 45°.

8. Thoroughly dehydrated sulphate of copper.

9. A one-half normal solution of potassium hydroxide in 95 per cent. redistilled alcohol.

10. A one-half normal solution of hydrochloric acid.

The method of procedure in making the determination is as follows: About 20 grams of the copper sulphate are measured off by means of a copper scoop made to hold that amount, and placed upon the bottom of the porcelain mortar. The surface is then somewhat depressed in the centre by the pestle. Ten cc. of milk, measured, or measured and weighed if great accuracy is required, are spread over the sulphate in such a way that none of it can come in contact with the porcelain. When the drying of the milk, which requires only a few minutes, is seen to be nearly complete, the mass is ground up, with the addition of a little clean sand, and transferred to the extraction tube. During the filling of the tube the side of it should occasionally be tapped, in order to render the mass compact. The Erlenmeyer flask is attached to the pump, and the mortar washed with three portions of the benzene, of from 10 to 15 cc. each, care being taken to allow each portion to filter through completely before another is added. Nine other portions of from 10 to 15 cc. of benzene are now poured into and drawn through the tube, the same precaution as to the complete filtration of each portion before the addition of another being observed. It is not certain that so large a number of extractions is necessary, but we have repeatedly assured ourselves that twelve such washings are sufficient to remove every trace of butter from the tube.

The flask is removed to the water-bath and the volume of the butter solution reduced by evaporation to 10 cc. or less, when 20 cc. of the one-half normal solution of caustic potassa are added. The flask is now returned to the water-bath and heated for fifteen minutes. Finally, the excess of alkali is determined by means of the one-half normal solution of hydrochloric acid, with use of phenol-phthalein as the indicator. We do not attempt to keep the alcoholic solution of alkali up to standard, but determine each day the number of cubic centimetres of it required to exactly neutralise twenty cubic centimetres of the acid solution, and add that volume to the flask for each saponification.

According to Koettstorfer,[1] the average amount of potassium hydroxide required to saponify one gram of butter is 227 milligrams; but the results of several experiments to determine the amount required to saponify the butter which had been extracted from the dried residue of milk and estimated by the usual gravimetric method, indicate that the number 230 is more correct. Hence that number has been employed in the calculation of the results here given.

Having found the volume of alkali solution required for the saponification, the quantity of butter which it represents is determined by multiplying by 28 (the number of milligrams of KOH in 1 cc. of the solution) and dividing by 230 (the number of milligrams required to saponify 1 gram of butter).

The following table gives a comparative statement, in percentages, of the results obtained by the analysis of five different specimens of milk. The quantity of milk was determined in every case by weighing. The first column, *a*, gives the percentages obtained by the usual gravimetric method of determining butter in milk; the second, *b*, those obtained by saponification of the butter thus determined; while the third, *c*, exhibits the results obtained by the method just described.

I.

a.	*b.*	*c.*
5.45 per cent.	5.40 per cent.	5.42 per cent.

II.

2.53 per cent.	2.57 per cent.	2.59 per cent.
...	...	2.61

III.

4.59 per cent.	4.71 per cent.	4.70 per cent.
...	...	4.58

IV.

4.13 per cent.	4.15 per cent.	4.28 per cent.
4.15	4.17	4.29

V.

3.75 per cent.	3.84 per cent.	3.84 per cent.
3.81	3.78	3.88

The agreement between the results obtained by the gravimetric method and those by the method here described is, at least, satis-

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[1] Zeitschrift für analyt. Chemie **18**, 199 and 431.

factory. The expeditiousness and simplicity of the method also recommend it.

A series of ten determinations was undertaken by Mr. W. M. Burton, of this laboratory, to whom we are much indebted for assistance in working out the method, in order to ascertain how many estimations a single analyst could be expected to complete within a given time. They were completed in less than four hours, with the following percentage results:

3.28, 3.21, 3.32, 3.25, 3.21, 3.25, 3.28, 3.28, 3.25, (3.36). The last result was vitiated by the presence of a small quantity of copper sulphate in the flask which had found its way through the cotton filter.

The collection of apparatus which we would recommend for the rapid execution of a large number of analyses consists of two such series of stands (of five each) as we have already described, ten flasks and extraction tubes, ten pipettes, not less than five mortars, two filter pumps, and a water-bath with holes enough to accommodate eight or ten flasks. With such conveniences and the requisite materials at hand, one analyst could easily complete from twenty-five to thirty determinations within a day of eight hours.

The method is still under examination with reference to the improvement of its details. The most advantageous change which, if it is practicable, could be made, relates to the concentration of the standard solutions. It is to be hoped that $\frac{1}{10}$ or $\frac{2}{10}$ normal solutions may be substituted for the $\frac{1}{2}$ normal ones now in use, and the exactness of the method thereby correspondingly increased.

Chemical Laboratory, Johns Hopkins University.

ON THE ADDITION OF SODIUM ACETACETIC ETHER AND ANALOGOUS SODIUM COMPOUNDS TO UNSATURATED ORGANIC ETHERS.

By Arthur Michael.

I.

In the synthesis of carbon derivatives, the methods generally in use start from saturated compounds, and the linking of carbon to

carbon takes place by substitution, addition, condensation, or polymerisation. The conversion of unsaturated compounds into saturated of a higher carbon series has been realised in several instances; but, especially in the fatty series, these are few in number, and have not led to a general method. Claus[1] has shown that allyl iodide, potassium cyanide and alcohol heated in a sealed tube give the nitrile of pyrotartaric acid, and believes that when α-chlorcrotonic acid is used, instead of allyl iodide, tricarballylic acid is formed.[2] He did not, however, succeed, in generalising the reaction.

We are indebted to Balsohn[3] for the interesting discovery that ethylene unites with benzene in the presence of aluminium chloride to form mono-, di- and triethylbenzene. Silva[4] has shown that allyl chloride, acting on the benzene-aluminium chloride mixture, gives diphenylpropane, and Essner[5] that amylene unites with benzene under the same conditions to form dimethyl-ethyl-phenyl-methane. This reaction was used by Demole[6] in an attempt to determine the constitution of α-dibromethylene, and Angelbis and Anschütz[7] have proved that when vinyl bromide instead of ethylene is used, a mixture of diphenylethane and dimethyl-anthracene-hydride is obtained. It is not unlikely that the Balsohn method is capable of further generalisation for the synthesis of aromatic hydrocarbons.

I shall describe in this paper a synthetical method of building up carbon derivatives by the direct union of carbon and sodium to unsaturated carbon atoms. This method is based on the property of unsaturated organic ethers of adding directly to sodium derivatives of organic compounds that contain the metal in direct union with carbon. In this reaction the metal unites with an unsaturated carbon, and the negative organic radical with the adjacent unsaturated carbon. It will be noticed that the reaction bears a strong analogy to the formation of halogen derivatives by the union of halhydric acids to unsaturated compounds, as in both reactions we have unsaturated compounds splitting up reagents into positive

[1] Annalen der Chemie **191,** 37.   [2] Berichte d. deutsch. chem. Gesell. **14,** 1084.
[3] Bull. Soc. Chim. **31,** 540.   [4] *Ibid.* **36,** 66.   [5] *Ibid.* **36,** 212.

[6] Demole considered that there is a direct substitution of bromine by phenyl, and therefore that the formation of unsymmetrical diphenylethylene in the reaction proved the constitution of α-dibromethylene. In a discussion of his work I showed that this interpretation is improbable, and that the first stage of the reaction probably consisted in an addition to form styrene-dibromide. (This Journal **5,** 193.)

[7] Berichte d. deutsch. chem. Gesell. **19,** 167.

and negative components to unite with them, forming saturated substances. I have endeavored, in the experiments described below, to select a few typical instances, in order to show the range and capability of the reaction.

Action of Sodium Malonic Ether on Ethyl Cinnamate.

The substances were used in molecular proportions : 4.6 grams sodium were dissolved in 50 grams absolute alcohol, and 32 grams malonic ether added to the solution. On adding the required amount of cinnamic ether (34 grams), it was noticed that the precipitate of sodium malonic ether soon went into solution that became slightly yellow. This solution was heated in a sealed tube in a water-bath for six hours, and then in an open vessel at 100° until the greater part of the alcohol was expelled. The residue was then mixed with water, acidified, extracted with ether, and the extract, after drying over calcium chloride, fractionated under ordinary pressure. It was found that very little unchanged malonic or cinnamic ether remained, and that the main product of the reaction went over between 305° and 310° under slight decomposition. The decomposition may be prevented by fractionating in a vacuum, when, under a pressure of 15 mm., it is easy to isolate a colorless, heavy oil boiling at 213°-215° (oil-bath, at 260° thermometer to 40° in vapor).

An analysis gave the following results :

0.2705 gram substance gave 0.6403 gram CO_2 and 0.1785 gram H_2O.

	Calculated for $C_{18}H_{24}O_6$.	Found.
C	64.29	64.55
H	7.10	7.32

The substance $C_{18}H_{24}O_6$ is formed by the direct union of cinnamic ether to sodium malonic ether, and replacement of sodium by hydrogen. These reactions are represented by the following equations :

$$C_6H_5 - CH - CH - COOC_2H_5 + NaHC - (COOC_2H_5)_2 =$$
$$C_6H_5 - CH - CHNa - COOC_2H_5$$
$$|$$
$$CH - (COOC_2H_5)_2$$

$$C_6H_5 - CH - CHNa - COOC_2H_5$$
$$| \qquad\qquad\qquad + H_2O =$$
$$CH - (COOC_2H_5)_2$$

$$C_6H_5 - CH - CH_2 - COOC_2H_5$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad + NaOH.[1]$$
$$\quad CH - (COOC_2H_5)_2$$

It was subsequently found that the reaction proceeds in the cold, and that even better results are thus obtained than by heating. A flask containing an alcoholic solution of cinnamic ether and sodium malonic ether was allowed to stand at ordinary temperature for five days, the contents of the flask then thrown into about five times its volume of water and extracted with ether. After evaporating the ether on a water-bath the residue was fractionated in a vacuum and was found to consist almost entirely of the new ether. To obtain the corresponding acid the ether was saponified with alkali. A mixture of 15 grams of the ether, 16 of caustic potash and 20 of water was heated on a water-bath, but no decomposition was noticed after heating an hour. It was then heated to boiling for about ten minutes, when the ether disappeared. The solution was acidified and extracted with ether, when, after evaporation of the solvent, an oily substance remained. This substance was probably an acid ether, notwithstanding the fact that a considerable excess of alkali was used. It was treated with a solution of 10 grams of caustic potash in an equal amount of water, when a violent reaction took place with the evolution of alcohol. To make sure that the saponification was complete the solution was kept at boiling for two hours. It was found more advantageous, however, to decompose the ether with barium hydrate. Eight grams of the ether were heated for several hours to boiling with a solution of 24 grams of the hydrate in 60 grams of water. The ether gradually disappeared, to make place for a white precipitate of the barium salt. This was dissolved in dilute hydrochloric acid, the barium removed by addition of sulphuric acid and filtration, and the filtrate extracted with ether. The heavy, oily substance that remained after the ether was driven off did not solidify, but when heated for a long time at 100° C. a constant but slow evolution of carbon dioxide took place, and the oil gradually became solid. This may be effected in a much shorter time by heating the oil to 110°–120°. The crystalline residue was purified by several crystal-

[1] In these equations it is assumed that the negative part of the additive compound takes the β-position towards the carboxyl—a supposition that is extremely probable. I shall endeavor, however, to furnish positive proof of the correctness of this view. The compound is the ether of β-phenyl γ-dicarboxyl-butyric acid.

lisations from a *small quantity of alcohol.* It gave on analysis the figures appended :

0.2529 gram substance gave 0.5686 gram CO_2 and 0.1350 gram H_2O.

0.2372 gram substance gave 0.5550 gram CO_2.

	Theory for $C_{11}H_{12}O_4$.	Found.	
C	63.81	64.19	63.77
H	5.76	5.99	

The acid crystallises in needles that are difficultly soluble in water, quite soluble in hot, moderately in cold alcohol. It melts at 137.5°–138.5° and has the constitution of a phenylglutaric acid, as is shown by the following equations :

$$C_6H_5-CH-CH_2-COOC_2H_5$$
$$|\qquad\qquad\qquad +3KOH=$$
$$CH-(COOC_2H_5)_2$$
$$\qquad\qquad C_6H_5-CH-CH_2-COOK$$
$$\qquad\qquad |\qquad\qquad\qquad +3C_2H_5OH;$$
$$\qquad\qquad CH-(COOK)_2 \diagdown$$

$$C_6H_5-CH-CH_2-COOH \qquad C_6H_5-CH-CH_2-COOH$$
$$|\qquad\qquad\qquad = \qquad |\qquad\qquad\qquad +CO_2$$
$$CH-(COOH)_2 \qquad\qquad CH_2-COOH.$$
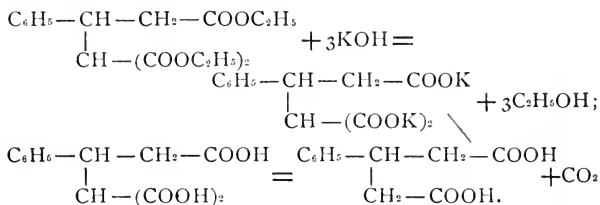
On addition of a solution of silver nitrate to a neutral solution of the ammonium salt of phenylglutaric acid a white, amorphous precipitate of the silver salt is obtained that is almost insoluble in hot water. It does not change on exposure to the light, and may be dried at 100° ; 0.6747 gram of air-dried salt did not change in weight on heating to 100° C., and gave 0.3443 gram silver.

	Calculated for $C_{11}H_{10}Ag_2O_4$.	Found.
Ag	51.18	51.32

The following qualitative reactions of the acid were obtained by adding solutions of the salts to an aqueous solution of the ammonium salt :

$CuSO_4$: Blue, amorphous precipitate, difficultly soluble in hot water.

$Pb(C_2H_3O_2)_2$: White, amorphous precipitate. On heating in presence of water, it is converted into bundles of small, truncated prisms, slightly soluble in water.

$HgNO_3$: A precipitate of white discs that are insoluble in hot water.

$Hg(NO_3)_2$: In the cold no change was noticed, but on heating the solution a granular precipitate was deposited.

$SnCl_2$: A precipitate of large, colorless, striated, flat prisms, with obliquely truncated ends, soluble in hot water.

$FeCl_3$: Amorphous, salmon-colored precipitate, insoluble in hot water.

Barium and magnesium chlorides gave no precipitate.

Action of Sodium Acetacetic Ether on Cinnamic Ether.

2.6 grams sodium were dissolved in 30 grams absolute alcohol, 14.8 grams acetacetic ether and finally 20 grams cinnamic ether were added. The solution was allowed to stand for five minutes, and then heated on the water-bath until the greater part of the alcohol was driven off. On treating the residue with water an oil remained undissolved that was removed by extracting with ether. The aqueous solution was then acidified, when a very heavy, oily substance separated, that gradually turned solid. A partial purification of this substance may be effected by extracting with ether immediately after acidifying, when it goes into solution, to partially separate soon after as white needles. The filtrate from these needles contained a notable amount of the substance that may be obtained by evaporation, or better by drying the solution with fused calcium chloride, when the substance is almost completely precipitated. For analysis it was purified by one crystallisation from dilute and two from strong alcohol.

0.2452 gram substance gave 0.6227 gram CO_2 and 0.1402 gram H_2O.

	Theory for $C_{15}H_{18}O_4$.	Found.
C	69.23	69.29
H	6.15	6.35

The substance crystallises from alcohol as long, white needles that melt at $140°-141°$. It is insoluble in water, quite soluble in alcohol, and moderately in moist ether, but almost insoluble in the latter solvent when dry. It possesses acid properties, dissolving in alkalies and hot solutions of the alkali carbonates. The formation of this compound may be represented as follows:

$$C_6H_5 — CH — CH — COOC_2H_5 + CH_3 — CO — CHNa —$$
$$COOC_2H_5 = C_6H_5 — CH — CHNa — COOC_2H_5$$
$$\mid$$
$$CH — COOC_2H_5 \qquad =$$
$$\mid$$
$$CO — CH_3$$

$$C_5H_5 - CH - CH - COOC_2H_5{}^1$$
$$ | | + NaOC_2H_5$$
$$ CH - CO$$
$$ |$$
$$ CO - CH_3.$$
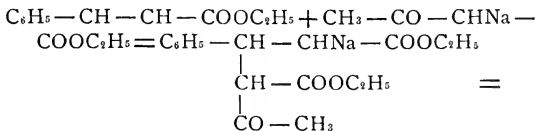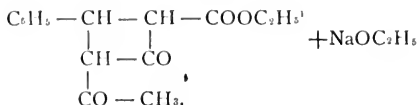
The silver salt was obtained by adding a solution of silver nitrate to a neutral solution of the substance in ammonia. It separated as radial clusters of small white prisms that are insoluble in water. The salt is extremely sensitive to exposure to the light, and decomposes when heated to 100° C.

0.6616 gram salt dried in a vacuum gave 0.1906 gram silver.

	Theory for $C_{15}H_{15}AgO_4$.	Found.
Ag	29.41	28.83

The following qualitative reactions were obtained by adding aqueous solutions of metallic salts to a neutral solution of the substance in ammonia: $Cu(NO_3)_2$: Green, amorphous precipitate, insoluble in hot water, but softening under it; $SrCl_2$: White precipitate of globular groups of small prisms, insoluble in hot water; $HgCl_2$: White, granular precipitate, insoluble in water; $Pb(NO_3)_2$: White, amorphous precipitate, moderately soluble in hot water, but softens under it when an insufficient amount of water is used; $FeCl_3$: Dark brown precipitate, difficultly soluble in hot water.

Barium and magnesium chlorides give no precipitate.

Action of Sodium Acetacetic Ether on Citraconic Ether.

It seemed of interest to ascertain whether the ethers of unsaturated fatty acids possess the property of adding to sodium acetacetic ether, and a few preliminary experiments with citraconic ether were made. To a solution of 2.6 grams of sodium in 30 grams of absolute alcohol, 15 grams of acetacetic ether, and then, after cooling, 21.4 grams of citraconic ether were added. The solution was heated on a water-bath until most of the alcohol was expelled, and the residue treated with water; an oil remained undissolved, and by acidifying a further quantity of an oily substance separated.

---

[1] This compound is isomeric with the cinnamyl acetacetic ether obtained by Fischer and Kuzel (Berichte d. deutsch. chem. Gesell. **16**, 166) by the action of cinnamyl chloride on sodium acetacetic ether. Experiments with this compound, and analogous substances from other unsaturated ethers, the results of which will be published later, show quite definitely that sodium and $COOC_2H_5$ when in the γ-position—and, as the following paper shows, also in the δ-position—have a great tendency to condense by eliminating C_2H_5ONa. I intend to follow up this subject, which promises extremely interesting results. I shall endeavor to bring further proof of the correctness of the formula given above.

The ethereal extract of this mixture contained two substances that were separated by repeatedly shaking with a solution of sodium carbonate. After drying the ethereal solution over calcium chloride, the ether was distilled off, and an attempt was made to fractionate part of the residue under ordinary pressure, but, as it decomposed considerably under these conditions, a pure substance was not obtained. The remainder was fractionated four times in a vacuum, when most of the liquid passed over between 170°–180°; and finally a colorless oil was obtained that boiled at 173°–174° under 26 mm. pressure (oil-bath, 235° thermometer to 40° in vapor).

0.2871 gram oil gave 0.6033 gram CO_2 and 0.1989 gram H_2O.
0.2861 gram oil gave 0.6056 gram CO_2 and 0.1992 gram H_2O.

	Theory for $C_{15}H_{24}O_7$.	Found.	
C	57.00	57.39	57.66
H	7.59	7.71	7.74

The neutral substance is formed by direct union of reagents:

$$C_3H_4 = (COOC_2H_5)_2 + CH_3CO - CHNa - COOC_2H_5 = C_{15}H_{23}NaO_7,$$

$$C_{15}H_{23}NaO_7 + H_2O = C_{15}H_{24}O_7 + NaOH.$$
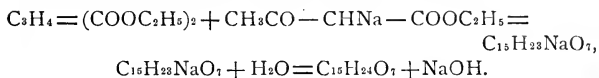
The alkaline solution obtained by shaking the ethereal solution of the products of the reaction with sodium carbonate contains a substance with acid properties that is precipitated as a heavy oil on addition of a mineral acid. This substance could not be obtained in a solid state, and an attempt to purify it by fractionation in a vacuum failed, as it underwent partial decomposition. It has an odor like that of crotonic acid, and doubtless corresponds to the acid substance obtained by the action of cinnamic ether on sodium acetacetic ether.

Action of Sodium Malonic Ether on α-Bromacrylic Ether.

The action of ethylene bromide on sodium or disodium malonic ether gives rise to the same compound, called by its discoverers vinaconic or trimethylene-dicarboxylic ether. According to Fittig,[1] the substance possesses the constitution of a vinylmalonic ether, $CH_2 - CH - CH(COOC_2H_5)_2$; while Perkin[2] considers it a

derivative of trimethylene $\begin{matrix} CH_2 - CH_2 \\ \diagdown \diagup \\ C - (COOC_2H_5)_2 \end{matrix}$. Somewhat later

[1] Fittig and Röder, Annalen der Chemie **227**, 13.
[2] Berichte d. deutsch. chem. Gesell. **17**, 53.

Conrad and Guthzeit[1] examined the behavior of a,β-dibrompropionic ether towards disodium malonic ether and obtained a compound that they considered, adopting the view of Perkin of the nature of these reactions, as trimethylene-tricarboxylic ether. The acid obtained by saponification decomposes on heating, forming what is called the trimethylene-dicarboxylic acid. Adopting Fittig's view of the constitution of vinaconic acid, the compounds of Conrad and Guthzeit are not derivatives of trimethylene, but unsaturated acids, and the dibasic acid has the same constitution as itaconic acid. They are, therefore, allo-isomeric.[2] This view of the reaction I attempted to prove by investigating the action of a-bromacrylic ether on sodium malonic ether, as the synthesis of Conrad's trimethylene-tricarboxylic ether in this way, judging from what was known at the time of the experiment, would conclusively prove that Fittig's view is the correct one. If we consider, however, that a-bromacrylic ether is an unsaturated substance, we shall have to take the newly discovered property that such substances have of adding to sodium malonic ether into consideration ; and no less than three constitutions are possible for the compound in question :

$$\text{I. } CH_2 — CBr — COOC_2H_5 + CHNa — (COOC_2H_5)_2 =$$
$$CH_2 — CH — (COOC_2H_5)_2.$$
$$|$$
$$CBrNa — COOC_2H_5$$

$$\begin{array}{l} CH_2 — CH — (COOC_2H_5)_2 \\ | \qquad\qquad\qquad\qquad + C_2H_5OH = \\ CBrNa — COOC_2H_5 \end{array}$$
$$CH_2 — CH —(COOC_2H_5)_2 + C_2H_5ONa =$$
$$|$$
$$CBrH — COOC_2H_5$$

$$a. \quad \begin{array}{l} CH — CH — (COOC_2H_5)_2 \\ | \qquad\qquad\qquad\qquad + C_2H_5OH + NaBr. \\ CH — COOC_2H_5 \end{array}$$

$$\begin{array}{l} CH_2 — CNa — (COOC_2H_5)_2 \\ | \qquad\qquad\qquad\qquad + C_2H_5OH = \\ CHBr — COOC_2H_5 \end{array}$$
$$\beta. \quad \begin{array}{l} CH_2 — C — (COOC_2H_5)_2 \\ | \diagup \qquad\qquad\qquad + C_2H_5OH + NaBr ; \\ CH — COOC_2H_5 \end{array}$$
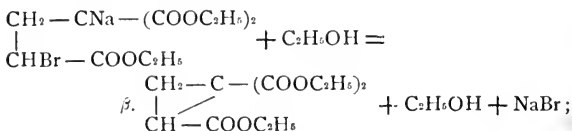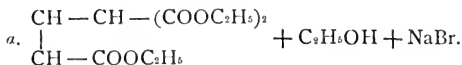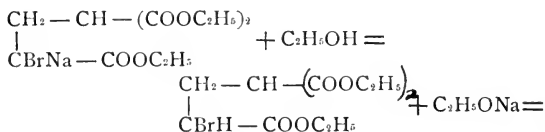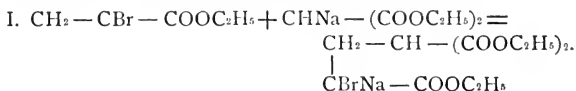
[1] Berichte d. deutsch. chem. Gesell. **17**, 1186.

[2] Michael, Berichte d. deutsch. chem. Gesell. **19**, 1385, 1378; **20**, 554; Michael and Browne, *ibid.* **19**, 1381; **20**, 550; Journal für prak. Chemie, [2] **35**, 257.

II. $CH_2 — CBr — COOC_2H_5 + CHNa — (COOC_2H_5)_2 =$

$$CH_2Na$$
$$|$$
$$CBr — CH — (COOC_2H_5)_2 =$$
$$|$$
$$COOC_2H_5$$

CH_2
$|$
$C — CH — (COOC_2H_5)_2 + NaBr.$
$|$
$COOC_2H_5$
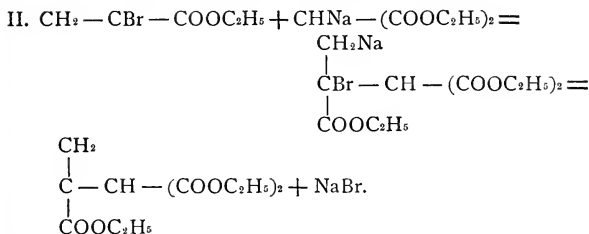
α-Bromacrylic ether was made by Wagner and Tollens[1] by the action of ethyl bromide on silver bromacrylate, but as this method does not give very satisfactory results, I made several experiments to obtain it in a different manner. A solution of αβ-dibrompropionic ether in absolute alcohol was treated with the equivalent quantity of sodium ethyl oxide, when a violent reaction took place, and sodium bromide was deposited. The alcoholic solution was treated with water, extracted with ether, and dried over calcium chloride. On fractionating this extract it is easy to isolate a heavy, oily, colorless liquid, that is insoluble in water, and boils from 202°–204° under slight decomposition. The bromine determinations gave the following figures:

I. 0.3576 gram liquid gave 0.3137 gram AgBr.
II. 0.3845 gram liquid gave 0.3379 gram AgBr.

	Theory for $C_7H_{13}O_3Br$.	Found.	
Br	37.3	37.05	37.14

The liquid is formed by replacement of bromine by ethoxyl, and is α-ethoxy-β-brompropionic ether :

$CH_2Br — CHBr — COOC_2H_5 + NaOC_2H_5 =$
$$CH_2Br — CH(OC_2H_5) — COOC_2H_5 + NaBr.$$
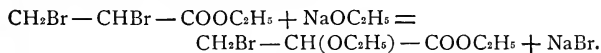
Another experiment was to heat dibrompropionic ether to a high temperature in a paraffin-bath. Heated somewhat below the boiling-point of the ether, an evolution of bromhydric acid took place, but it was found impossible to isolate α-bromacrylic ether from the resulting product. These experiments having failed, I returned to the method of Wagner and Tollens, that I found of advantage to slightly modify. The silver salt and an excess of ethyl bromide were heated in a closed tube for six hours at 100°, and the

tube was then opened, connected with a condenser and heated on a
water-bath until the excess of the bromide was expelled. The
apparatus was now connected with an air-pump, the air exhausted
from it, and the tube heated in a Meyer's air-bath as long as a
liquid passed over. On fractionating the distillate in a vacuum it
is easy to isolate a light oil that distils without decomposition
between $75°$-$77°$ under 33 mm. pressure.

0.4551 gram substance gave 0.4875 gram of AgBr.

	Theory for $CH_2 - CBr - COOC_2H_5$.	Found.
Br	44.7	45.53

Ten grams of a-bromacrylic ether were gradually added to a
solution of sodium malonic ether, prepared by adding a solution of
1.1 grams of sodium in absolute alcohol to 7 grams of malonic ether.
The reaction was violent, and the solution gave no alkaline test
after it had stood a short time. The flask containing the product
of the reaction was heated on a water-bath until most of the alcohol
was driven off, the residue mixed with water and extracted with
ether. On fractionating, after the ether had passed over, the
thermometer rose very rapidly to $270°$, when, between that temper-
ature and $280°$, almost the entire product of the reaction dis-
tilled. By fractionating this liquid[1] several times, it was easy to
separate a fraction, that formed the greater part of the original
liquid, boiling between $276°$–$277°$. On analysis this portion gave
the result as below :

	Theory for $C_{12}H_{18}O_6$.	Found.
C	55.81	55.60
H	7.00	7.34

The ether obtained from a-bromacrylic ether and sodium malonic
ether agrees exactly in its properties with the compound obtained
by Conrad and Guthzeit from a,β-dibrompropionic ether and di-
sodium malonic ether ; but, in order to give further proof of the
identity of the two products, the first-named ether was saponified,
and the acid so obtained compared with that described by Conrad
and Guthzeit. The decomposition of the ether by aqueous sodium

[1] I have used for upwards of a year a slightly modified Hempel column that deserves a brief
description. A round glass bulb that goes loosely into the neck of the fractionating flask, and
is open at both ends, is attached to a piece of thin platinum wire and suspended from the top of
the flask so that it is half-way in the neck and round part. The neck is then almost filled to
the lateral tube with beads, and the distillation effected as usual. It is astonishing how much
sharper a few inches of beads will cause a separation of two liquids than without their use.
By using a long-neck boiling flask, a good Hempel column can be arranged in the flask.

hydrate gave an acid which, though finally obtained pure, is difficult to purify. A better result is obtained by decomposing with barium hydrate. For this purpose the ether was boiled several hours, in a flask with a reverse condenser, with a concentrated aqueous solution of three times the theoretical quantity of base. As the ether was decomposed the insoluble barium salt of the acid was deposited. A sufficient quantity of chlorhydric acid to dissolve the salt was then added, the barium precipitated by sulphuric acid, and the filtrate repeatedly extracted with ether. On evaporation of the ether an oil remained that gradually solidified. Instead of crystallising from water and ether, it is more advantageous to purify by several crystallisations from glacial acetic acid. The acid obtained in this way melts between $184°-185°$, under evolution of carbonic anhydride. It is obtained from water as hard, glittering prisms, forming concentric groups, with end faces, which are sometimes not well defined, giving a navicular shape to the crystals. I also made the acid according to the method of Conrad and Guthzeit, and found that the properties of their product correspond exactly with those which I have just described. The neutral solutions of the acid in ammonia also gave the same qualitative tests on addition of various salts. These experiments seem to me to prove quite conclusively that α-bromacrylic ether and sodium malonic ether[1] and α,β-dibrompropionic ether and disodium malonic ether react to form the same compound.

According to Perkin, vinaconic ether does not contain a hydrogen that can be substituted by sodium. It seemed of interest to examine trimethylene-tricarboxylic ether in its behavior towards sodium ethyl oxide and alkyl halogens, and it was found that the ether obtained by using α,β-dibrompropionic ether gave the same result as that made with α-bromacrylic ether. On adding the ether to an absolute alcoholic solution of sodium ethyl oxide, the reagents being used in equivalent proportions, the solutions turned slightly yellow, which would seem to indicate that the ether contains a hydrogen replaceable by sodium. If such a compound be formed,

[1] The bromine estimation of α-bromacrylic ether given above is somewhat high; and as it might seem that the so-called trimethylene-tricarboxylic ether was formed from some $\alpha\beta$-dibrompropionic ether contained in it, I mention the quantitative results obtained in my experiment. Ten grams α-bromacrylic ether gave seven grams of ether boiling between $276°-277°$, and three or four grams that were almost pure. If the bromacrylic ether contained 5 per cent. of the dibromether, the bromine percentage would have been increased 1 per cent., and only one gram of the ether boiling at $277°$ could have been formed. The high bromine percentage is undoubtedly caused by a trace of bromhydric acid that I found impossible to remove by distillation.

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it is certainly very unstable, as by allowing ethyl iodide or benzyl chloride to react on the solution—although a separation of sodium iodide or chloride took place slowly in the cold, more rapidly on heating, and it lost its alkaline reaction—nothing but unchanged trimethylene-tricarboxylic ether could be isolated.

It evidently follows from the results described in this paper that the so-called trimethylene-tricarboxylic ether may possess one of three different constitutions, and to none of these can a decided preference be given at present.

In the present paper only unsaturated ethers were examined in which the unsaturated carbons are in the α- and β-position towards the carboxylic ether group. I shall make the behavior of other classes of unsaturated ethers and of the bromalkylenes the subject of a future paper.[1]

Tufts College, College Hill, Mass.

ON SOME NEW REACTIONS WITH SODIUM ACET-ACETIC AND SODIUM MALONIC ETHERS.

By Arthur Michael.

Although sodium acetacetic ether and analogous sodium compounds have been the starting-points of almost innumerable researches and have yielded some of the most interesting syntheses known in organic chemistry, it would seem as if the view presented in the preceding paper—that is, the dual nature of these compounds —has been overlooked. The results obtained by treating these sodium compounds with unsaturated organic ethers suggested the desirability of examining their behavior towards organic reagents that have the property of uniting with substances with weakly combined negative and positive components. This investigation has yielded such an extensive, in fact almost unlimited, field of investigation, that I deemed it desirable to publish a preliminary note on the results already obtained, reserving a full account of the work and its continuation for a future paper.

[1] It would also be of interest to examine the behavior of the sodium derivative of nitro-ethane towards unsaturated ethers.

Behavior towards Aldehydes.—Claissen[1] has found that by treating a mixture of an aldehyde and acetacetic or malonic ether with dehydrating agents a series of new compounds is formed with elimination of water. An entirely different series of compounds is obtained by allowing aldehydes to react on the sodium derivatives of these ethers. Thus, by allowing an alcoholic solution of benzoic aldehyde and sodium acetacetic ether to stand for a day, a compound crystallising in flat prismatic plates of the composition $C_{22}H_{22}O_7$ is formed:

$$C_6H_5CHO + CH_3COCHNa - COOC_2H_5 = C_{13}H_{15}NaO_4;$$
$$2C_{13}H_{15}NaO_4 = C_{22}H_{20}Na_2O_7 + (C_2H_5)_2O.$$
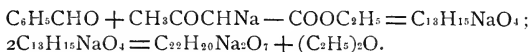
This compound melts at $126°$–$127°$ and is soluble in alkalies, while the compound obtained according to the method discovered by Claissen melts at $59°$ and is insoluble in alkalies.

Behavior towards Ketones.—This class of compounds does not react in the cold, but on heating at $100°$ in a closed tube crystalline salts are deposited. The reaction has not been further examined.

Behavior of Mustard Oils.—The alkyl and aromatic mustard oils unite very readily with sodium acetacetic and malonic ethers to form mono-thio-amides. Thus, by mixing phenyl mustard oils with alcoholic sodium malonic ether the latter compound goes immediately into solution, and soon rhombic prisms separate that have the composition $C_{14}H_{15}NaSNO_4$. By treating this salt with an acid the thio-anilide is obtained that crystallises in long yellow needles melting at $59\frac{1}{2}°$–$60°$:

$$CHNa - (COOC_2H_5)_2 + C_6H_5NCS = CH{\diagup}^{CSNNaC_6H_5}_{\diagdown(COOC_2H_5)_2};$$
$$CH{\diagup}^{CSNNaC_6H_5}_{\diagdown(COOC_2H_5)_2} + HCl = CH{\diagup}^{CSNHC_6H_5}_{\diagdown(COOC_2H_5)_2}.$$
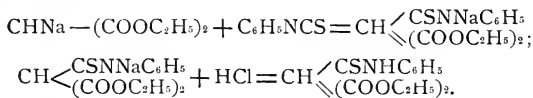
Behavior of Phenyl Isocyanate.—These reactions are more complicated than those of the corresponding mustard oils. In its action on sodium acetacetic ether two products and on the malonic salt three products are formed. The isocyanate reacted very violently on sodium malonic ether. After standing some hours the white salt was separated by filtration, and the filtrate acidified. The oil that separated solidified partially on standing, and the solid substance,

[1] Annalen der Chemie **218**, 12, 129 and 170; also Hantzsch, Berichte d. deutsch. chem. Gesell. **18**, 2579.

after crystallisation from alcohol, melted at 123°–124°, and is the mono-anilide of methenyl-diethyl-tricarboxylate:

$$CHNa - (COOC_2H_5)_2 + C_6H_5NCO = CH \underset{\diagdown (COOC_2H_5)_2.}{\overset{\diagup CONNaC_6H_5}{}}$$

The white salt yielded after treating with acids a compound crystallising in orange plates, and melting at $171\frac{1}{2}°$–172°. Its composition is expressed by the formula $C_{12}O_3H_9N$, and it is probably formed from the preceding substance by splitting off of alcohol and water:

$$C_{14}O_5H_{17}N = C_{12}O_3H_9N + H_2O + C_2H_6O.$$

Behavior of Anhydrides of Bibasic Organic Acids.—The substances unite immediately, forming carbonyl acids. Thus, on mixing a warm alcoholic solution of phthalic anhydride with alcoholic sodium acetacetic ether the solution turns solid on cooling. From the sodium salt, by treating with an acid and extracting with ether, a heavy oil is obtained that was dried in a vacuum at 100°. This substance has acid properties, and decomposes at 140° into phthalic anhydride and acetacetic ether. Its composition is $C_{14}H_{14}O_6$:

$$C_6H_4\underset{\diagdown CO}{\overset{\diagup CO}{}}O + CH_3 - CO - CHNa - COOC_2H_5 =$$
$$C_6H_4\underset{\diagdown COONa}{\overset{\diagup CO - CH}{}}\underset{\diagdown COOC_2H_5.}{\overset{\diagup CO - CH_3}{}}$$
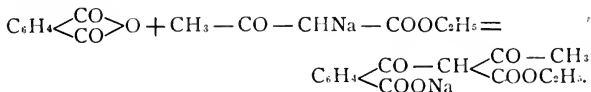
Behavior of Inorganic Anhydrides.—Carbon dioxide passed through an alcoholic solution of sodium malonic ether causes a precipitate of the compound $CH\underset{\diagdown (COOC_2H_5)_2}{\overset{\diagup COONa}{}}$;

$$CO_2 + CHNa = (COOC_2H_5)_2 = CH\underset{\diagdown (COOC_2H_5)_2.}{\overset{\diagup COONa}{}}$$
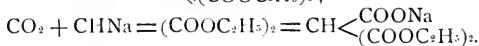
This salt is very unstable, as even cold water decomposes it into malonic ether and sodium bicarbonate. Carbon bisulphide reacts immediately on sodium malonic ether, forming a yellow salt. Acids precipitate from a solution of the salt a heavy oil with a disagreeable odor:

$$2CHNa(COOC_2H_5)_2 + CS_2 =$$
$$CNa\underset{\diagdown (COOC_2H_5)_2}{\overset{\diagup CSSNa}{}} + CH_2(COOC_2H_5)_2.$$
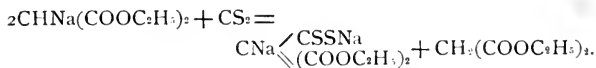
Sulphur dioxide and sodium malonic ether also give a precipitate, that appears to consist of sodium ethyl sulphate :

$$CHNa = (COOC_2H_5)_2 + SO_2 + C_2H_5OH =$$
$$CH_2 = (COOC_2H_5)_2 + SO{<}^{OC_2H_5}_{ONa}.$$
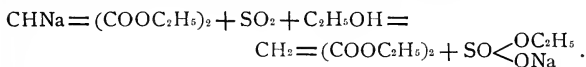
A different result is obtained by treating solid sodium malonic ether suspended in benzene with sulphur dioxide. Under these conditions apparently a sulphinate is formed. Phosphorus pentoxide also acts on sodium malonic ether under the same conditions.

Behavior of Phenols.—By dehydrating a mixture of resorcin and acetacetic ether with zinc chloride, Schmid[1] obtained a beautifully fluorescent body, which he named resocyanine. The correct formula of this substance was afterwards ascertained by v. Pechman and Duisberg[2] and by myself.[3] Wittenberg[4] obtained similar compounds from other phenols and acetacetic ether, and v. Pechman and Duisberg proved that the substances belong to the coumarine series. The same class of derivatives is obtained by allowing an alcoholic solution of phenols and sodium acetacetic ether to stand in the cold. A solution of resorcinol in sodium acetacetic ether soon became fluorescent, and, after standing several days, it was diluted with water and acidified, when a copious precipitate of resocyanine or β-methylumbelliferone was formed. This reaction is remarkable on account of the condensations that take place in the cold:

$$C_6H_4{<}^{OH}_{OH} + CH_3 - CO - CHNa - COOC_2H_5 =$$

$$C_6H_3 \begin{cases} OH \\ OH \\ COH - CHNa - COOC_9H_5 = \\ | \\ CH_3 \end{cases}$$

$$C_6H_3 \begin{cases} OH \\ ONa \\ COH - CH_2 - COOC_2H_5 = \\ | \\ CH_3 \end{cases}$$

$$C_6H_3 \begin{cases} OH \\ O\overline{} \\ C - CH - CO + NaOC_2H_5 + H_2O. \\ | \quad | \\ CH_3 \end{cases}$$
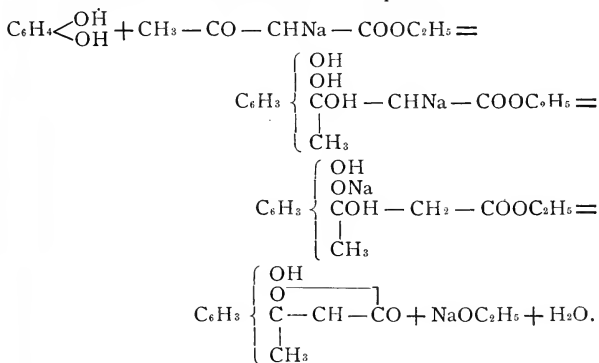
[1] Journal f. praktische Chemie [2], **25**, 81.
[2] Berichte d. deutsch. chem. Gesell. **16**, 2119; v. Pechman and Cohen, *ibid.* **17**, 2129.
[3] This Journal **5**, 434. [4] Journal f. praktische Chemie [2], **26**, 66.

While working on resocyanine, I endeavored to make similar derivatives from resorcinol and malonic ether by means of zinc chloride, but was unable to obtain any results. By the action of resorcinol and sodium malonic ether a fluorescent compound is formed that has not as yet been further examined.

Behavior of Sulphur.—Flowers of sulphur dissolve in the cold in alcoholic sodium malonic ether, but apparently no reaction takes place. On heating this solution to 100° a crystalline precipitate is formed that when treated with acids gives a heavy oil, with a strong mercaptane odor.[1] This oil undoubtedly represents the thiotartronic ether:

$$CHNa = (COOC_2H_5)_2 + S = CHSNa = (COOC_2H_5)_2.$$
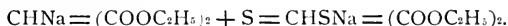
Behavior of Ureas.—Sodium acetacetic and malonic ethers react on carbamides to form the corresponding ureides. As an example, the action of carbamide on sodium malonic ether may be mentioned. The finely powdered substance dissolves in alcoholic sodium malonic ether, and presently the solution becomes solid. This precipitate is the sodium salt of barbituric acid, which may be obtained from it by treating it with acids:

$$CHNa - (COOC_2H_5)_2 + CO(NH_2)_2 =$$
$$CHNa{<}^{CO-NH}_{CO-NH}{>}CO + 2C_2H_5OH.$$
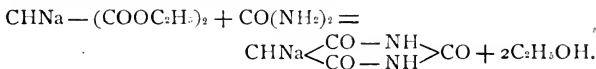
Behavior of Sulpho-urea.—This compound acts like urea to form the corresponding sulpho-derivatives. Thus, from sulpho-urea and sodium malonic ether a crystalline precipitate is formed that consists of sodium sulpho-barbiturate. The free acid forms rhombic plates, that decompose at a high temperature without melting:

$$CS(NH_2)_2 + CHNa - (COOC_2H_5)_2 =$$
$$CHNa{<}^{CO-NH}_{CO-NH}{>}CS + 2C_2H_5OH.$$
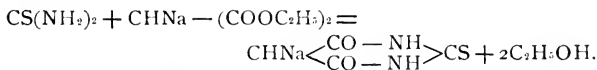
Behavior of Amides.—Sodium derivatives, formed by elimination of alcohol, are deposited. Acetamide dissolves readily in alcoholic sodium malonic ether, in proportion of two molecules of the first to one of the second compound, and the solution soon solidifies. This compound crystallises in prisms and has the composition $C_7O_4N_2Na_2H_8$:

$$2CHNa - COOC_2H_5 + 2CH_3 - CONH_2 = C_7Na_2N_2H_8$$
$$+ CH_2 - (COOC_2H_5)_2 + 2C_2H_5OH.$$

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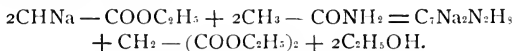
[1] Sulphur dissolves in malonic ether and gives off hydrogen sulphide on boiling.

Behavior of Aldehyde-ammonia.—As in the preceding reaction, condensation-products containing sodium are formed. Aldehyde-ammonia dissolves readily in alcoholic sodium acetacetic ether, and in a few minutes the solution becomes solid. The substance, which crystallises in long, fine, white needles in alcohol, has the composition $C_8H_{12}O_2NNa$:

$$CH_3 - CH{<}^{OH}_{NH_2} + CH_3 - CO - CHNa - COOC_2H_5 =$$
$$C_8H_{16}O_4NNa; \quad C_8H_{16}O_4NNa = C_8H_{12}NaO_2N + 2H_2O.[1]$$
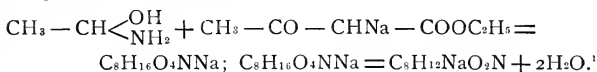
I have made some other tests with sodium acetacetic and malonic ethers, and find that these reagents react on lactones, amidines, primary bases, guanidine, cyanamide, cyanic acid and benzoquinone. The above-described reactions will also be tried with sodium derivatives containing two atoms of sodium in their molecule, and with the sodium derivates of the nitro-alkanes.

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[1] The four last reactions are probably caused by the formation of derivatives having stronger acid properties than the original substances, and the formation of sodium compounds that are insoluble in alcohol. In order to test this hypothesis, I have made some experiments on the action of a mixture of oxalic ether and sodium ethylate on urea, phenylhydrazine, guanidine and aldehyde-ammonia, and find that this mixture acts exactly as sodium acetacetic or malonic ethers. The addition of oxalic ether to a solution of urea in alcoholic sodium ethylate immediately causes a dense white precipitate, which is the sodium derivative of parabanic acid:

$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + CO{<}^{NH_2}_{NH_2} + NaOC_2H_5 = CO{<}^{NH - CO}_{NNa - CO} + 3C_2H_5OH.$$
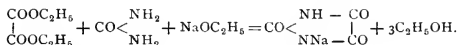
By using phenylhydrazine a precipitate consisting of prisms is formed. This has the composition of $C_8H_8N_2NaO_3$:

$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + C_6H_5N_2H_3 + C_2H_5ONa = \begin{matrix} CO - N_2H_2C_2H_5 \\ | \\ COONa \end{matrix} + 2C_2H_5OH.$$
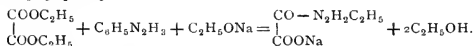
Guanidine and sodium ethylate treated with oxalic ether gave a heavy white precipitate containing 34 per cent. sodium. The salt treated with acids gives a crystalline substance which decomposes at a high temperature, and is almost insoluble in all solvents. This compound has the constitution $C_3N_3H_3O_2$, and is oxalylguanidine:

$$HN - C{<}^{NH_2}_{NH_2} HSCN + \begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + NaOC_2H_5 =$$
$$NH - C{<}^{NH - CO}_{NH - CO} + NaSCN + 3C_2H_5OH.$$
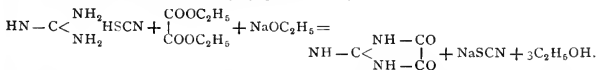
Other organic reagents behave in presence of sodium ethylate in a similar manner, as experiments with sulpho-urea, cyanamide, amidines and hydroxylamine have shown. There is no doubt that weakly defined basic or acid substances act as strong bases in the presence of sodium ethylate. Not alone oxalic ether acts in this manner, but carbonic, benzoic, succinic, and tartaric ethers act in the presence of sodium ethylate on most of the above reagents, forming new compounds. It is very likely that all organic ethers that do not undergo a change when mixed with sodium ethylate will give similar reactions. It has also been found that mixtures of sodium ethylate and weak bases behave towards certain other reagents as strong bases. This research will be continued.

ON THE ACTION OF ALDEHYDES ON PHENOLS.
III.[1]

BY A. MICHAEL AND J. P. RYDER.

In an earlier paper it was shown that benzoic aldehyde in the
presence of a trace of a mineral acid acts on resorcinol, forming the
resinous compound $C_{26}H_{20}O_4$, which is easily converted by mineral
acids into an isomeric crystalline substance. In the present paper
we have made the behavior of a number of aldehydes towards
phenols the subject of a similar investigation.

Behavior of Benzoic Aldehyde towards Phenol.

Benzoic aldehyde heated with phenol does not act on it, but a
reaction takes place when a small amount of hydrochloric acid is
present. A solution of 15 grams phenol, 13.3 grams benzoic alde-
hyde, and five drops of hydrochloric acid dissolved in 20 grams of
alcohol, was heated in an atmosphere of carbon dioxide for about an
hour, and afterwards treated with steam in order to expel any un-
changed aldehyde or phenol. A resinous substance remained
behind, which we were unable to crystallise. For analysis it was
dissolved in glacial acetic acid, and the solution poured into water,
an operation which was repeated several times. The resin was dried
in a vacuum at 100° and was analysed, with the following results:

0.211 gram substance gave 0.657 gram CO_2 and 0.102 gram H_2O.

	Theory for $C_{26}H_{20}O$.	Found.
C	85.71	84.90
H	5.49	5.37

The resin when pure is white, but a slight exposure to the air is
sufficient to color it somewhat. The substance analysed was
slightly colored, which accounts for the noticeable difference
between the percentages indicated by theory and those obtained
from the analysis. That, however, this substance has the above
formula was shown by preparing its acetyl derivative. For this
purpose 2 grams of the resin, 4 grams of acetic anhydride, and 1
gram of fused sodium acetate were heated on a water-bath, and
then treated with water. The white, amorphous product was

purified by dissolving in acetic acid and precipitation by water. It gave the following numbers:

0.407 gram substance dried in a vacuum at 100° gave 1.119 grams CO_2 and 0.205 gram H_2O.

	Theory for $C_{26}H_{18}O_2(OCCH_3)_2$.	Found.
C	80.26	79.71
H	5.40	5.59

We were unable by treatment with acid to convert the resin into a crystalline substance. Distilled with zinc dust, a small amount of high-boiling hydrocarbons was obtained, but a fractional distillation of these products failed to isolate a homogeneous substance.

The resin is formed according to the equation :

$$2C_6H_6O + 2C_6H_5CHO = C_{26}H_{20}O_2 + 2H_2O.$$

Action of Benzoic Aldehyde on Pyrogallol.

The reaction between benzoic aldehyde and pyrogallol in the presence of considerable hydrochloric acid was examined by v. Baeyer,[1] who obtained, when operating in the cold, the resinous substance $C_{26}H_{22}O_7$, and in the heat an isomeric crystalline compound. The formation of this substance from two molecules of the aldehyde and phenol under elimination of a molecule of water did not conform with our experiences in the similar resorcinol reaction ; but as v. Baeyer used a large quantity of strong acid, we thought the difference might be due to that fact. We therefore repeated v. Baeyer's experiment, and the results of our analyses lead us to change the constitution of the crystalline substance.

Pyrogallol and benzoic aldehyde were dissolved in absolute alcohol, the air of the vessel expelled by carbon dioxide, and concentrated hydrochloric acid added in small quantities. The first of the two following analyses was made with a portion of the substance formed as soon as acid was added to the solution, while for the second the compound obtained by adding considerable acid was crystallised from acetone. In each case the substance was dried in an atmosphere of carbon dioxide *in vacuo* at 100°, and the dry products were perfectly white.

I. 0.181 gram substance gave 0.479 gram CO_2 and 0.0795 gram H_2O.

II. 0.220 gram substance gave 0.585 gram CO_2 and 0.096 gram H_2O.

[1] Berichte d. deutsch. chem. Gesell. **5**, 25, 280.

Theory for v. Baeyer's Formula, $C_{26}H_{22}O_7$.	Theory for $C_{26}H_{20}O_6$.	Found. I.	Found. II.
C	69.95	72.89	72.41	72.54
H	4.92	4.67	4.91	4 85

That the substance possesses the composition $C_{26}H_{20}O_6$ was further confirmed by preparing and analysing its acetyl derivative. For this purpose it was treated with acetic anhydride and sodium acetate at 100° C., and the product of the reaction crystallised from glacial acetic acid. An analysis gave the following numbers:

0.241 gram substance, dried at 100° in the air, gave 0.591 gram CO_2 and 0.104 gave H_2O.

Theory for $C_{26}H_{14}O_6(OCCH_3)_4$.	For v. Baeyer's Formula, $C_{26}H_{16}O_7(C_2H_3O)_6$.	Found.
67.05	62.75	66.88
4.70	4.78	4.79

The compound forms white, truncated prisms that may be heated to 100° C. in the air without change.

We have also convinced ourselves by experiments that the same substance is formed by treating the alcoholic aldehyde-pyrogallol solution with a small amount of acid; and that the formation of the crystalline substance is preceded by that of an amorphous substance, which by heating with acid is changed into the crystalline isomeride. In fact the reaction is strictly analogous to that of resorcinol, although with pyrogallol it was found that relatively more acid is required to form the resin, and also for its conversion into the crystalline modification.

Action of Benzoic Aldehyde on Phloroglucinol.

A drop of hydrochloric acid added to a boiling alcoholic solution of the phenol and aldehyde causes an immediate precipitate of a resinous compound which is quite insoluble in alcohol. For analysis it was dissolved in hot alcohol, and the precipitate obtained by cooling dried at 100° in a vacuum.

0.221 gram substance gave 1.586 grams CO_2 and 0.092 gram H_2O.

	Theory for $C_{26}H_{20}O_6$.	Found.
C	72.89	72.31
H	4.67	4.62

The resin is very susceptible to oxidation, turning quickly red in the air. We were unable to convert this substance into the

crystalline modification. An alcoholic solution treated with a considerable quantity of acid gave unchanged resin.

Action of Benzoic Aldehyde on Orcinol.

Ten grams of orcinol, 8.5 of aldehyde, 15 of absolute alcohol and two drops of hydrochloric acid were heated for a short time, and the solution thrown into water. The white resin that was precipitated was purified by dissolving in alcohol and precipitating with water. For analysis it was dried in carbon dioxide at 100°.

0.232 gram resin gave 0.672 gram CO_2 and 0.120 gram H_2O.

	Theory for $C_{22}H_{24}O_4$.	Found.
C	79.23	78.95
H	5.66	5.76

Like most of the analogous compounds, it is easily oxidised in the air. This resin could not be converted into a crystalline compound. It was found to remain unchanged even when boiled with strong hydrochloric acid.

Qualitative Experiments on the Behavior of Phenols towards Aldehydes.

In the following experiments the phenol and aldehyde were dissolved in absolute alcohol and a small quantity of hydrochloric acid was added. Hydroquinol and benzoic aldehyde do not react in the cold, but after heating the solution the addition of water precipitates a resin.

Eugenol and Benzoic Aldehyde.—No reaction even on boiling the solution and adding a considerable amount of acid.

α-Naphthol and Benzoic Aldehyde.—Violent reaction in the cold. On pouring into water a resin was precipitated.

β-Naphthol and Benzoic Aldehyde.—Converted into a resin after standing some hours.

Hydroquinol and Ethyl Aldehyde.—No resin formed in the cold, but on heating.

Eugenol and Ethyl Aldehyde.—No resin formed in the cold nor in the heat.

Pyrogallol and Ethyl Aldehyde.—No reaction in the cold. On heating a resin is formed.

Resorcinol and Butyric Aldehyde.—Resin formed in the cold.

Resorcinol and Valeric Aldehyde.—Resin formed in the cold.

Resorcinol and Œnanthol.—Resin formed in the cold. Could not be converted into a crystalline substance.

Resorcinol and Cinnamic Aldehyde.—Immediate reaction in the cold. The resin remained unchanged on further treatment with acid.

Resorcinol and Cuminol.—Resin formed in the cold that is convertible into a crystalline substance consisting of square plates.

Resorcinol as a Reagent for the Detection of Aldehydes.

The above-described experiments, together with those described in the former paper on this subject, show that an absolute alcoholic solution of resorcinol containing a trace of hydrochloric acid would be a valuable reagent for detecting aldehydes of monobasic acids, if no other analogous substances show a similar behavior. We have examined chloral hydrate, acetone, benzophenone, butyrone, acetacetic ether, acetophenone, mesoxalic and pyruvic acids, in regard to their behavior towards the resorcinol solution, and find that no reaction takes place in the cold, even if considerable acid is added. No reaction takes place when succinic or phthalic anhydrides or dextrose and levulose are added to the solution.

In testing for an aldehyde we recommend a solution of one part of resorcinol in two of absolute alcohol, then the addition of a small amount of the substance to be tested, and finally a few drops of strong hydrochloric acid. If no resin is formed, the solution, after standing several hours, is poured into water, when, if the substance contains an aldehyde, a resinous or crystalline precipitate should be formed.[1] This test is of special interest, inasmuch as it distinguishes an aldehyde from a ketone, while such reagents as hydroxylamine and phenylhydrazine give tests for both these groups of substances. By combining the resorcinol test with one of the above, it may be ascertained whether the substance contains a ketone, as, if a substance gives the two last tests and not the first, it must evidently be due to the presence of a ketone.

Action of Chloral Hydrate on Orcinol.

In the second paper[2] on the action of aldehydes on phenols, it was shown that chloral hydrate and resorcinol, in aqueous solution, react in the heat to form a substance free of chlorine. This

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[1] We have not tried the reaction on other classes of aldehydes.   [2] This Journal **5**, 349.

substance is so unstable towards oxygen that a colorless specimen could not be obtained for analysis, and the formula deduced from the analytical results was open to some doubt. We thought it likely that the corresponding orcinol derivative would show a greater stability, and that its analysis might be of value in ascertaining the constitution of the resorcinol compound.

A solution of ten parts orcinol, five parts chloral hydrate in forty parts of water was heated to boiling, in a flask with a reversed condenser, and in an atmosphere of carbon dioxide, as long as the deposition of a crystalline substance was noticed. The precipitate was dissolved in hot dilute alcohol, treated with boneblack, and purified by several crystallisations. The substance was dried in a vacuum at $100°$, and was very nearly white. On analysis it gave the numbers given below:

I. 0.212 gram substance gave 0.502 gram CO_2 and 0.101 gram H_2O.

II. 0.207 gram substance gave 0.488 gram CO_2 and 0.099 gram H_2O.

	Theory for $C_{23}H_{24}O_8$.	Found. 1.	Found. II.
C	64.25	64.58	64.33
H	5.13	5.29	5.34

The compound crystallises from alcohol in white needles, which are insoluble in hot water, readily soluble in strong alcohol. It oxidises in the air, but is more stable than the resorcinol compound. By treating it at $100°$ with acetic anhydride and fused sodium acetate, an acetyl derivative was obtained. This substance was purified by crystallisation from alcohol, and melts at $185°$. For analysis it was dried in the air at $100°$.

0.196 gram gave 0.458 gram CO_2 and 0.090 gram H_2O.

	Theory for $C_{35}H_{34}O_{13}$.	Found.
C	63.42	63.73
H	5.13	5.10

The formation of a substance having the position $C_{23}H_{24}O_8$ from orcinol and chloral hydrate may be explained by assuming that the chlorine of the chloral hydrate acts on the hydrogen of the benzene nucleus, and the reaction may be represented as follows:

$$CCl_3CH(OH)_2 + 3C_6H_3(OH)_2CH_3 =$$
$$C[C_6H_2(OH)_2CH_3]_3 - CH(OH)_2 + 3HCl.$$
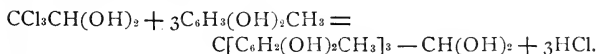
The substance may be considered as derived from the unstable ethylidene hydrate by the replacement of hydrogen by orcinolyl, and may be named triorcinolylethylidene hydrate. The action of acetic anhydride consists not alone in the introduction of acetyl, but also in dehydration :

$$C[C_6H_2(OH)_2CH_3]_3CH(OH)_2 + 7(C_2H_3O)_2O = \\ C[C_6H_2(OOCCH_3)_2CH_3]_3 - CHO + 8CH_3COOH.$$
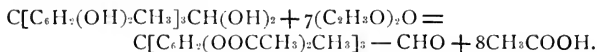
These results induced us to analyse the resorcinol derivative again. We were unable to obtain a product that was not somewhat oxidised, owing to its great avidity for oxygen.

0.168 gram gave 0.394 gram CO_2 and 0.063 gram H_2O.

0.158 gram gave 0.3705 gram CO_2 and 0.062 gram H_2O.

	Theory for $C[C_6H_2(OH)_2]_3 - CH(OH)_2$.	Found.	
C	62.18	63.94	63.98
H	4.66	4.17	4.36

We are inclined to think that the discrepancy between the results indicated by theory and those obtained from analysis is due to the impossibility of obtaining a substance not partially oxidised. This view is corroborated by comparing the results obtained from the analysis of the perfectly stable derivative formed by the action of acetic anhydride and those required by theory :

	Calculated for $C[C_6H_3(OOCCH_3)_2]CHO$.	Found.	
C	61.93	61.71	61.70
H	4.51	4.32	4.67

An experiment was made to oxidise the acetyl derivative of the resorcinol compound. 2.5 grams of the substance were dissolved in cold acetic acid, and .66 gram of potassium permanganate, also in solution, gradually added. After standing 24 hours the solution was poured into water, and the precipitate thus formed crystallised several times from acetic acid.

0.221 gram, dried at 100° in the air, gave 0.509 gram CO_2 and 0.081 gram H_2O.

	Theory for $C_{20}H_{16}O_8$.	Found.
C	62.5	62.8
H	4.1	4.1

The substance crystallises in prisms that are insoluble in alcohol and water and melt at about 210°. It may be supposed to be formed by the oxidation of formyl into carboxyl and replacement of acetyl by hydrogen :

$$C_{20}H_{16}O_x = C[C_6H_3(OH)_2]COOH.$$
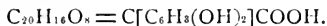
Before this view can be wholly accepted a more detailed examination of the substance is necessary.[1]

TUFTS COLLEGE, COLLEGE HILL, MASS.

[1] Herr L. Claissen has recently published a paper (Berichte d. deutsch. chem. Gesell. **19,** 3316, and Annalen der Chemie **237,** 261), from v. Baeyer's laboratory, on the action of aldehydes on phenols, in which he takes occasion to criticise my work and publicly call attention to supposed negligence on my part in not acknowledging work done in the same laboratory. I gather from his remarks that Herr Claissen deems it proper to criticise the work of other chemists without becoming acquainted with their papers. At least, I can think of no other explanation of Herr Claissen's attitude in regard to my work, as every research that had been published on the subject in question from v. Baeyer's laboratory is given even a detailed mention in my paper (this Journal **5,** 338). Herr Claissen will find on consulting my paper that I have not relied on the proximate analyses of the resorcinol-benzoic aldehyde compounds to settle their constitution. Although the new formula he suggests for the resorcinol-benzoic aldehyde compound has a carbon and hydrogen percentage that approximates those obtained by analysis, the acetyl-derivate of such a compound differs very considerably in its carbon percentage from what was actually obtained, as will be seen from the following :

	Theory for Claissen's Formula of Resorcinol Compounds, $C_{19}H_{14}O_3$.	For my Formula, $C_{26}H_{20}O_4$.	Found. I.	II.	III.
C	78.62	78.69	78.32	78.83	78.78
H	4.81	5.05	5.27	5.62	5.51

	Theory for Acetyl-derivate of Claissen's Formula, $C_{19}H_{12}O_3(C_2H_3O)_2$.	For Acetyl-derivate of my Formula, $C_{26}H_{16}O_4(C_2H_3O)_4$.	Found.	
C	73.79	72.34	72.16	72.31
H	4.75	4.93	5 48	5.17

	Theory for Claissen's Formula of Pyrogallol Compound, $C_{19}H_{12}O_5$.	This Formula Less One Mol. of Water, $C_{19}H_{10}O_4$.	For Baeyer's Formula, $C_{26}H_{22}O_7$.	For my Formula, $C_{26}H_{20}O_6$.	Found.	
C	70.80	75.00	69.95	72.89	72.41	72.54
H	4.34	3.75	4.92	4.67	4.91	4.85

	Theory for Claissen's Formula of Acetyl Derivative, $C_{19}H_8O_6(C_2H_3O)_4$.	Acetyl Derivative of $C_{19}H_{10}O_4$, $C_{19}H_6O_4(C_2H_3O)_2$.	Acetyl Derivative of Baeyer's Formula, $C_{26}H_{16}O_7(C_2H_3O)_6$.	Acetyl Derivative of my Formula, $C_{26}H_{14}O_6$ $(C_2H_3O)_6$.	Found.	
	66.39	71.50	62.75	67.05	66.88	
	4.09	3.71	4.78	4.70	4.79	

The figures speak for themselves, and I should make no further mention of the matter if Herr Claissen had not announced his intention to repeat my work. I should be pleased to have him do this, but I wish that he would consult my paper before he publishes his results, so as to prevent any further misrepresentation of my work on his part. Herr Claissen will find that my work was not done with a view of mere compound-making ; that the work he has in view, and many other suggestions on the subject, were clearly stated a number of years before he began his work, and also that, until I published my research, the subject I examined rested on an entirely false basis. Nobody who takes the trouble to read the literature on the subject of aldehyde-phenol-condensation can for a moment doubt that those condensations that take place in so dilute an acid solution that the reactions might be used as tests for traces of mineral acids are different in their nature from those requiring the strongest known dehydrating agents, especially as entirely different results are obtained by using the different methods.

REVIEWS AND REPORTS.

Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre. Edited by Wilh. Ostwald and J. H. van't Hoff. Leipsic. 12 numbers to the volume.

The interesting results derived from a so-called "cross-fertilisation of the sciences" are nowhere more apparent than in the field covered by both chemistry and physics. The phenomena of heat, light, electricity, vapor tension, crystallisation and density have all contributed to the problems of chemical energy; and the interest in these researches has so extended in late years that the new journal must find a cordial welcome. The editors (who have shown marked ability in quantitative experimental research, as well as mathematical analysis) are the authors of a "Lehrbuch der allgemeinen Chemie" and "Études de Dynamique chimique"; and these representatives of Russia and Holland at the head of a German periodical suggest the cosmopolitan character of science.

The first two numbers were issued in February and March. An introductory note quotes the remark of Du Bois-Reymond that "physical chemistry may be called the chemistry of the future." The journal is supplementary to Ostwald's text-book of "general chemistry"; for this, he says, in contrast to the special chemistry of the several kinds of matter, "is not merely a limb, but the sap of the tree."

The ninety-six pages already issued are chiefly devoted to original papers, the general purpose of which may be gleaned from the following summary:

P. C. F. Frowein. "Dissociation of Salts containing Water of Crystallisation." The vapor tensions of partly dehydrated salts are determined, and discussed in the light of thermodynamics.

O. Lehmann. "Crystallisation of Mixtures." After an historical introduction, and brief reference to his former debate with Dr. Brügelmann, a description is given of crystals of the four ethers: $C_6H_4O_2(CO.O.C_2H_5)_2$, $C_6H_4O_2(CO.O.C_2H_5)_2$, $C_6H_2(OH)_2(CO.O.C_2H_5)_2$ and $C_6(OH)_4(CO.O.C_2H_5)_2$; besides crystals containing each one mixed with each of the others.

L. F. Nilson and *Otto Pettersson.* "Physical Constants of Germanium and Titanium." The mean value for the atomic heat of Ti was normal from 0° to 211°, but lower from 0° to 100°, and much higher at 301.5° or 440°; that of Ge was nearly constant, a unit below normal, within the same range of temperatures. Determinations of vapor density showed a partial dissociation of Ge I₄ at 658°, and probably of Ge S at a white heat. The critical temperature of Ge Cl₄ was 276.9°; and the vapor tension was determined for various temperatures.

D. Konowalow. "Theory of Fluids." The formula published by Van der Waals in 1881 to express "the continuity of the gaseous and fluid conditions" is discussed in regard to more recent experimental data and shown to be approximately correct.

W. Ostwald. "Nature of Chemical Affinity." Of the two isomeric nitrosalicylic acids, that having the constitution COOH : OH: $NO_2 = 1 : 2 : 3$ is decidedly stronger than that represented by 1 : 2 : 5. The hydroxyl is ortho and the nitro group is meta to carboxyl in both cases ; hence the difference can only depend upon the different relations of the nitro and hydroxyl groups to each other.

D. Konowalow. "Decomposition of Tertiary Amyl Acetate." In continuation of the author's investigation of "contact action," he shows that the presence of acetic acid promotes the separation of the ether into this acid and amylen. Menschutkin's determinations of the speed of dissociation (1882) are thus explained.

Robert Schiff. "Coefficient of Expansion of Gases, as Quantitative Lecture Experiment." Description of apparatus, with cut.

St. Gniewosz and *Al. Walfisz.* "Absorption of Gases by Petroleum." The coefficients at 10° and at 20° for H, N, O, N_2O, C_2H_4, CO_2, CO, and CH_4 were determined ; and at 20° nearly all were much *higher* than the coefficients for absorption by water ; hence, a layer of petroleum seems to afford no adequate "protection" to aqueous solutions.

W. Meysztowicz. "Salts of Pyrosulphurous Acid." Those of Ca, Sr, Ba and Mg could not be obtained.

W. Ostwald. "Electro-chemical Studies. Fifth Paper : Law of F. Kohlrausch." The former papers (Jour. pr. Chem. 1884–1886) showed that the molecular conductivity of monobasic acids increases with dilution, and seems to approach the same maximum value with all the acids examined. Several hundred new determinations are now published, embracing fifteen acids and their salts, at different degrees of dilution. These show essential differences among the acids, but confirm Kohlrausch's theorem [Wied. Ann. **6**, 167, (1879)] that the conductivity of a salt is the sum of two constants, depending upon the nature of the acid and the base respectively. The mean value for the molecular conductivity of sodium salts is 21.1 higher than for the corresponding salts of potassium under like conditions of dilution; the conductivity of lithium salts being 9.7 higher still. Further data are promised, extending the observations to weaker acids. R. B. WARDER.

Among the numerous smaller publications in the German language on the analysis of urine, the one by Hofmann and Ultzmann

occupies a deservedly high place. Its popularity in this country is attested by the appearance of a second edition of the English translation. In this later edition the necessary additions have been supplied to keep pace with the advances made during the past few years in the methods of analysis and the semiology of the urine.

Clearness of expression and the literary style show a marked improvement over the previous edition, although here and there the German idiom still persists.

The part descriptive of the normal and abnormal constituents of the urine with the qualitative tests is admirable. However, under the qualitative tests for albumen, the degree of delicacy of the picric acid test (Galippe's test) is stated to be above that of the nitric acid or the potassium ferrocyanide test. Laache, of Christiania, who made a thorough study of these tests, concludes that the nitric acid and the potassium ferrocyanide tests are of equal value, and that the picric acid test is considerably below them in delicacy.

Picric acid is also given as a test for glucose. The fact that picric acid in the presence of a caustic alkali produces similar claret-red colorations with either glucose or creatinine, and that it has even been brought forward as a delicate test for the latter in the urine, would hardly commend its employment as a good test for glucose.

Heller's or Moore's test is given as " the simplest and best test " for glucose. As the coloring matters in the urine so often interfere with this test, we may, by its performance, have the presence of glucose indicated in many urines which are entirely free from glucose.

Sufficient importance does not seem to have been given the tests for glucose with alkaline copper solutions.

To determine whether Fehling's solution has undergone decomposition, and is thereby unfit for use, it is advised simply to boil the Fehling's solution itself, neglecting to state that before boiling it should be diluted with about four volumes of water. Decomposition may have occurred in the Fehling's solution and without dilution before boiling would not become evident. This neglect is a fruitful source of error.

It is unfortunate that the methods for the preparation of the volumetric solutions are not given more in detail. Possessing the required standard solutions, the actual analysis is easily performed, as the methods for the latter are excellently and clearly described. It would, however, require a decidedly better knowledge of chemistry than is possessed by the average physician to prepare the standard solutions from the meagre descriptions given in the book, and also to accurately standardise them with solutions of known strength—which latter procedure is entirely omitted in this work.

The part devoted to the semiology of the urine is excellent, and must be of much value to the physician, while the plates showing the microscopic appearance of some of the normal and abnormal substances occurring in the urine cannot be excelled.

<div align="right">John Marshall.</div>

NOTES.

Apparatus for Filling a Burette.

The difficulty of filling a burette with standard solutions without a material loss of strength from evaporation has suggested to me the following plan: In Fig. 1, A is a glass tube bent as shown, and extending to the bottom of the bottle C containing the standard solution; B is a similar tube extending just beneath the stopper;
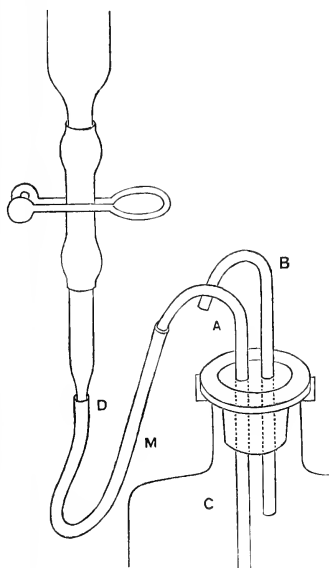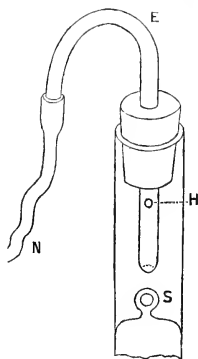
FIG. 1.   FIG. 2.

both tubes are sealed in the bottle after it is filled. A small rubber tube 30 cm. or 40 cm. long fits at either end on the glass tubes A and B, and remains in this position when the bottle is not in use. When the burette is to be filled the rubber tube is detached from B and slipped over the tip of the burette at D, thus leaving B open for the admission of air when the fluid is drawn from the bottle.

In Fig. 2, E is a bent glass tube fitted by means of a stopper to the top of the burette; it is pierced by a hole, H, in the side, just beneath the lower surface of the stopper, and extends about 2 cm. beyond, being open at each end; a rubber tube is attached to its outer end for the purpose of making suction with the mouth.

The bottle being attached by means of the rubber tube M to the tip of the burette, and the compressor being open, the fluid is drawn by suction on the tube N through the tube A, together with some air, into the burette. If a swimmer is not used, the air-bubbles will simply rise to the top and give no further trouble. With a swimmer, however, it will be necessary to remove them by drawing the swimmer forcibly against the bottom of the tube E (Fig. 2), when they will pass by the swimmer and escape; if not at the first trial, by allowing the swimmer to recede slightly and repeating the operation, the air will easily pass out. The object of extending E (Fig. 2) beneath the stopper, and of the lateral hole in E, is to prevent the solution from entering the suction tube N. When the burette is free from bubbles the fluid may be allowed to recede until the swimmer stands at the mark. The rubber tube M (Fig. 1) is detached from the burette and restored to its place on the tube B, thus sealing the bottle against any possible evaporation. The efficacy of the apparatus in preventing loss of strength is evident; in practice, I have found this method more speedy than any other I have known.   C. L. PENNY.

STATE NORMAL SCHOOL, SHIPPENSBURG, PA.

SOME PIECES OF CHEMICAL APPARATUS.

Simple, Portable, Quick-Filtering Apparatus.—The accompanying cut represents a quick-filtering apparatus devised by the
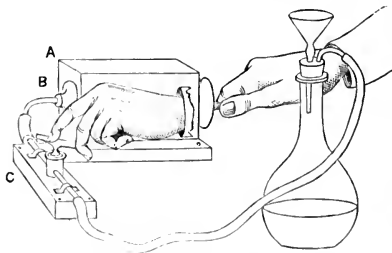
writer some four or five years ago, and which, in the absence of a head of water, answers fully all the purposes of the Bunsen pump. B is an ordinary hard rubber syringe, 5 inches long, fixed in a block, A (which is a piece of pump stock with a bore to suit the diameter of the syringe, and screwed to the table); and C is a three-way stopcock worked with the left hand while the right hand works the piston of the syringe.

The idea was suggested by the text of Fleischer's volumetric analysis, Muir's translation, pp. 28 and 29, and the translator's note, p. 269, where devices inferior to this are described.

Sulphuretted Hydrogen Apparatus without Stray Fumes.—
Kipp's apparatus is in every laboratory. When the apparatus is
not in use, the acid is above the iron sulphide, and gravity tends
to produce leakage. I put ferrous sulphide into the top instead
of the middle globe, having filled the stem with broken porcelain.
The bottom globe and one-half of the middle globe are then filled
with dilute acid. To the tubulure of the middle globe (through
which the gas is usually evolved) a rubber stopper, tube, and
pinchcock are attached. By blowing through the tube the acid
is made to ascend to the top globe, where it meets the iron sulphide.

When the gas is no longer needed, the pinchcock is opened
and the acid falls. The evolution tube is connected with a wash-
bottle, and the considerable difference of height renders regurgi-
tation impossible.

Obviously, in the absence of Kipp's apparatus, the same principle
can be variously applied. For example, a long bottle, say an inch
and a half in diameter, may have its bottom cut off and a one-
hole rubber stopper one and a half inches in diameter inserted. This,
on being inverted, may take the place of the top globe of Kipp's
apparatus, if a one-hole stopper and long tube be attached to the
neck, and if another bottle with a two-hole stopper (one of the
holes for the blowing-tube) be used as the acid reservoir.

*Simple Arrangement for Reverse Filtration (Carmichael's
Plan).*—The neck of an ordinary vial is cut off. The outer end
is ground on a lead, copper or wooden surface with emery and
water. Into the other end a one-hole rubber stopper is inserted,
and pushed in so as to be flush with the opposite end. On
the last-mentioned end a perforated platinum disc and a disc of
moistened filter paper are placed. Into the hole of the rubber
stopper a tube is inserted which is itself connected with the aspi-
rator. WOODVILLE LATHAM.

UNIVERSITY OF MISS., *January* 13, 1887.

On the Oxygen Acids of Iodine.

In an elaborate paper recently published, C. W. Blomstrand
shows that the periodates, which are generally regarded as pecu-
liar and inexplicable compounds, are easily understood if they are
referred to an acid H_5IO_6 or $IO(OH)_5$. In this compound, and in
all the periodates, the iodine is heptavalent. With caustic soda peri-
odic acid forms a salt of the formula $Na_2O_2.IO(OH)_3$, just as phos-
phoric acid forms the salt $Na_2O_2.PO(OH)$. And just as phos-
phoric acid forms with silver a salt in which all its hydrogen is
replaced by metal—viz. PO_4Ag_3—so periodic acid forms the salt
$IO(OAg)_5$ with silver.

The fact that the potassium salt of periodic acid has the com-
position KIO_4 is explained by assuming that this is a dehydration
product of the salt $KO.IO(OH)_4$; thus:

$$KO.IO(OH)_4 - 2H_2O = KO.IO_3.$$
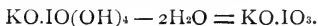
This phenomenon is analogous to that of the formation of sodium pyrophosphate from disodium phosphate:

$$\begin{matrix} Na_2O_2PO.OH \\ Na_2O_2PO.OH \end{matrix} - H_2O = \left. \begin{matrix} Na_2O_2PO \\ Na_2O_2PO \end{matrix} \right\} O.$$
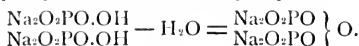
The fact that the change in the case of the periodate takes place at ordinary temperatures, while that of the phosphate requires comparatively high heat, is no evidence that the action in the two cases is essentially different.

Ordinary sodium periodate, $Na_2O_2IO(OH)_4$, when heated to 180° to 220° undergoes a change more strictly analogous to that of the phosphate as indicated in the two equations:

(1) $\qquad Na_2O_2IO\dfrac{(OH)_2}{(OH)_2} - H_2O = Na_2O_2IO \left\{ \begin{matrix} O \\ OH \end{matrix} \right.;$

(2) $\qquad \begin{matrix} Na_2O_2IO \left\{ \begin{matrix} O \\ OH \end{matrix} \right. \\ \\ Na_2O_2IO \left\{ \begin{matrix} OH \\ O \end{matrix} \right. \end{matrix} - H_2O = \begin{matrix} Na_2O_2IO \\ \\ Na_2O_2IO \end{matrix} \left\{ \begin{matrix} O \\ O \\ O \end{matrix} \right. = Na_4I_2O_9 .$
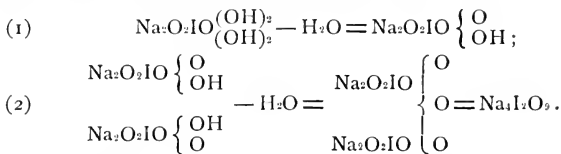
The salt $Na_4I_2O_9$ is thus seen to be closely related to ordinary sodium periodate.

Attention is called to the difference between perchloric and periodic acids, a difference which is like that between phosphoric and nitric acids. The normal form of perchloric acid is $HClO_4$ or $HO.ClO_3$, in which the chlorine is probably heptavalent. Evidently chlorine cannot hold in combination as many hydroxyls as iodine can, though both are heptavalent. So, too, in nitric acid the nitrogen is probably quinquivalent $HO.NO_2$, as phosphorus is in phosphoric acid, but the nitrogen cannot hold as many hydroxyls in combination as phosphorus can. A comparison of the formulas will bring this out more clearly:

$$\begin{matrix} HO.NO_2 & \qquad & (HO)_3PO \\ HO.ClO_3 & \qquad & (HO)_5IO . \end{matrix}$$

The principal periodates which have been described are those derived from acids belonging to the following series:

(1) Ortho $\qquad (HO)_5IO$ or $(HO)_2IO(OH)_3$.

(2) Di $\qquad \begin{matrix} (HO)_4IO \\ (HO)_4IO \end{matrix} \Big\} O$.

(3) Meso $\qquad (HO)_3IO.O$ or $\begin{matrix} (HO)_3IO \\ (HO)_3IO \end{matrix} \Big\} O_2$.

(4) Dimeso $\qquad \begin{matrix} (HO)_2IO \\ (HO)_2IO \end{matrix} \Big\} O_3$.

(5) Meta $\qquad (HO)IO.O_2$.
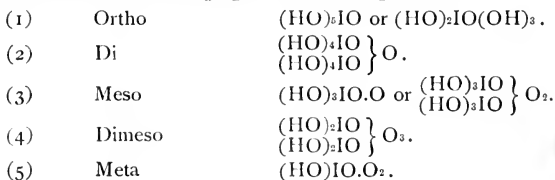
A number of periodates which have been described are shown to be derived from acids of the above formulas.—(*Journal für praktische Chemie* **34**, 433.)

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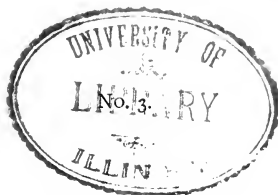
F. W. C.

AMERICAN

CHEMICAL JOURNAL.

LI.—ON MUCOXYBROMIC AND MUCOXYCHLORIC ACIDS.[1]

By Henry B. Hill and Arthur W. Palmer.

The action of baric hydrate upon mucobromic acid was studied several years ago by O. R. Jackson and one of us.[2] It was found that mucobromic acid was decomposed by a large excess of baric hydrate with the formation of a,β dibromacrylic and formic acids, while an essentially different reaction ensued in a feebly alkaline solution. The main product in this case was shown to be a dibasic acid containing four atoms of carbon; but it was not further studied. Somewhat later, E. K. Stevens and one of us[3] found that mucophenoxybromic acid was formed by an analogous reaction when mucobromic acid was treated with potassic phenylate; and the constitution of this acid was established with little difficulty by its conversion into phenoxybrommaleic and phenoxybromacrylic acids. The great stability of the latter acid in alkaline solution left no doubt that its structure was represented by the formula
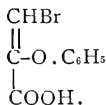
$$
\begin{array}{l}
\text{CHBr} \\
\| \\
\text{C--O . C}_6\text{H}_5 \\
| \\
\text{COOH.}
\end{array}
$$

I I

While it was thus rendered probable that in the corresponding decompositions by baric hydrate an atom of bromine in the muco-bromic acid had been replaced by hydroxyl, and the empirical formula of the product formed also warranted this conclusion, it was difficult to obtain any definite experimental evidence in its support. The isomerism of this acid with monobrommaleic and monobromfumaric acid, and its strongly marked dibasic character, made its constitution a question of decided interest. We therefore undertook its more extended investigation, as well as a study of the analogous chlorine compound, which could readily be obtained from mucochloric acid. Although our investigations are in many respects incomplete, they seem to us to leave little doubt as to the constitution of the compounds in question ; and since we shall be unable to continue the work together, we have thought it best to present the results which we have already obtained.

Mucoxybromic Acid.

Whenever mucobromic acid is dissolved in a solution of an alkaline hydrate, more or less mucoxybromic acid appears to be formed. For its preparation, however, we have found it necessary to use baric hydrate, and the yield is then largely dependent upon the conditions under which the reaction takes place. We have found it most advantageous to suspend the mucobromic acid in thirty parts of cold water, and, after cooling well with ice, to add gradually, with constant shaking, finely powdered baric hydrate of known strength. After the mucobromic acid is neutral-ised, the baric hydrate must be added in small quantities, and the solution allowed to stand until the alkaline reaction has nearly disappeared before a fresh portion is added. The alkaline reaction disappears rapidly at first, afterwards more slowly, and when the amount of baric hydrate demanded by the equation

$$2C_4H_2Br_2O_3 + 3BaO_2H_2 = 2BaC_4HBrO_4 + BaBr_2 + 4H_2O$$
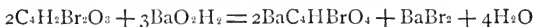
has been added, the reaction usually remains feebly alkaline, even after long standing. The slight excess of baric hydrate is then removed by carbonic dioxide, and an equal volume of alcohol added to the filtered solution. Baric mucoxybromate, which is very sparingly soluble in dilute alcohol, is thus precipitated in the form of fine, flattened, pointed needles, and may be purified by dissolving in cold water and reprecipitating with alcohol. With

careful work, about sixty per cent. of the theoretical yield may be obtained. The preparation of the free acid from the barium salt is a matter of considerable difficulty, since it cannot be extracted from aqueous solution by the ordinary solvents, and it is quickly decomposed during the evaporation of its solution, even at ordinary temperatures. We succeeded in preparing it only by moistening the salt with a little water, precipitating the barium exactly with sulphuric acid, and evaporating the concentrated solution of the acid thus obtained as rapidly as possible over sulphuric acid in vacuo. The viscous residue thus obtained gradually solidified at low temperatures, and yielded tolerably well-formed thick prisms with beveled ends. The substance, freed from the viscous mother liquors as completely as possible and dried over sulphuric acid, gave, on analysis, the following results:

I. 0.7181 gram substance gave 0.6451 gram CO_2 and 0.1004 gram H_2O.

II. 0.7504 gram substance gave 0.6697 gram CO_2 and 0.1010 gram H_2O.

III. 0.2053 gram substance gave 0.1977 gram AgBr.

IV. 0.2348 gram substance gave 0.2254 gram AgBr.

	Calculated for $C_4H_3BrO_4$.	I.	II.	III. Found.	IV.
C	24.60	24.50	24.34		
H	1.54	1.55	1.50		
Br	41.03	...	...	41.00	40.86

Mucoxybromic acid is extremely soluble in water, alcohol, or ether, and almost insoluble in chloroform, benzol, ligroin, or carbonic disulphide. The melting point was found to be $111°–112°$; the true melting point may, however, be somewhat higher, since the substance could not be purified by repeated crystallisation. The acid gives with ferric chloride an intense garnet-red coloration, which is readily seen, even in very dilute solutions. With argentic nitrate it gives a white crystalline precipitate of the silver salt. Baric acetate added to a concentrated aqueous solution throws down the highly crystalline barium salt. By the action of hydrobromic acid saturated at 0°, or of phosphoric pentabromide, no definite products were obtained.

Baric Mucoxybromate, $BaC_4HBrO_4.2H_2O$.—The preparation of the barium salt has already been described. The salt is somewhat sparingly soluble in cold water, and its solubility is not sensibly

increased by heat. It is rapidly decomposed by boiling its aqueous solution, and even in the cold decomposition ensues after long standing. On the evaporation of a solution saturated at ordinary temperatures over sulphuric acid in vacuo, the salt separates in long lustrous six-sided prisms with perpendicular terminations. The air-dried salt loses over sulphuric acid, or at 100°, rather more than one molecule of water, and has then the composition $BaC_4HBrO_4.H_2O$. When heated to 105°–115°, it slowly loses the second molecule of water, but at the same time it turns brown, and baric bromide is formed.

I. 1.5527 grams of the salt, crystallised from water and dried by exposure to the air, lost over sulphuric acid 0.0953 gram H_2O.

II. 1.0746 grams of the salt, precipitated by alcohol and dried by exposure to the air, lost over sulphuric acid 0.0663 gram H_2O.

III. 1.0502 grams of the salt, precipitated by alcohol and dried by exposure to the air, lost over sulphuric acid 0.0631 gram H_2O.

	Calculated for $BaC_4HBrO_4.2H_2O$.	I.	Found. II.	III.
$1H_2O$	4.92	6.14	6.17	6.01

The salt dried over sulphuric acid gave, on analysis, the following results :

I. 0.2769 gram of the salt gave 0.1837 gram $BaSO_4$.

II. 0.2052 gram of the salt gave 0.1368 gram $BaSO_4$.

III. 0.5470 gram of the salt gave 0.3678 gram $BaSO_4$.

IV. 0.4128 gram of the salt gave 0.2079 gram CO_2 and 0.0354 gram H_2O.

V. 0.4988 gram of the salt gave 0.2516 gram CO_2 and 0.0477 gram H_2O.

VI. 0.2120 gram of the salt gave 0.1128 gram $AgBr$.

VII. 0.2684 gram of the salt gave 0.1457 gram $AgBr$.

	Calculated for $BaC_4HBrO_4.H_2O$.	I.	II.	III.	Found. IV.	V.	VI.	VII.
Ba	39.37	39.00	39.19	39.54				
C	13.77	...	...	...	13.74	13.76		
H	0.86	...	...	...	0.95	1.06		
Br	22.99	...	...	...	...	...	22.64	23.11

We have made many unsuccessful attempts to prepare an acid barium salt. In every case, when the acid solution was precipitated with alcohol, or evaporated in vacuo over sulphuric acid, we obtained only the neutral salt.

Potassic Mucoxybromate, $K_2C_4HBrO_4.H_2O$.—The potassium salt was prepared from the barium salt by exact precipitation with potassic carbonate, and evaporation of the solution thus obtained in vacuo. It crystallised in well-formed rhombic plates, which were very soluble even in cold water. On warming the solution, decomposition quickly ensued. The air-dried salt lost nothing over sulphuric acid, turned somewhat brown at 70°, but did not lose sensibly in weight until heated to 100°.

I. 0.4951 gram of the air-dried salt lost, at 100°, 0.0344 gram H_2O, and gave 0.2991 gram K_2SO_4.

II. 0.4604 gram of the air-dried salt lost, at 100°, 0.0307 gram H_2O, and gave 0.2780 gram K_2SO_4.

III. 0.5428 gram of the air-dried salt gave 0.3281 gram K_2SO_4.

	Calculated for $K_2C_4HBrO_4.H_2O$.	I.	Found. II.	III.
K	27.04	27.12	27.10	27.14
H_2O	6.64	6.95	6.67	

Argentic Mucoxybromate, $Ag_2C_4HBrO_4$. — Argentic nitrate added to a solution of the free acid, or one of its salts, throws down a crystalline precipitate of the silver salt. When this is warmed with water, argentic bromide is at first formed, then reduction takes place. When heated in a slightly ammoniacal solution, it is immediately blackened. It dissolves readily in dilute nitric acid, but the solution soon grows turbid with the separation of argentic bromide. The dry salt explodes on heating, or on moistening with concentrated nitric acid. For analysis, the salt was made by precipitating an excess of argentic nitrate with a dilute solution of the barium salt.

I. 0.3974 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr, 0.3634 gram AgBr.

II. 0.5478 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr, 0.5034 gram AgBr.

III. 0.5455 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr, 0.4999 gram AgBr.

IV. 0.5866 gram of the salt dried in vacuo over H_2SO_4 gave, on heating in sealed tube with diluted nitric acid, 0.2672 gram AgBr.

	Calculated for $Ag_2C_4HBrO_4$.	I.	Found. II.	III.	IV.
Ag	52.82	52.53	52.78	52.64	
Br	19.56	...	...	...	19.38

A solution of the barium salt yielded, with plumbic nitrate, a heavy yellow semi-crystalline precipitate, which, when dried over sulphuric acid, gave on analysis percentages of lead and bromine which only approximated those required by the formula PbC_4HBrO_4.

Dimethyl Mucoxybromate, $C_4HBrO_4(CH_3)_2$.—The dimethyl ether of mucoxybromic acid can readily be formed by the action of methyl iodide upon the dry silver salt. If the methyl iodide is slowly added to the silver salt, so much heat is evolved that a violent and even dangerous explosion ensues. The silver salt must therefore be added in small portions to an excess of methyl iodide, or must be suspended in dry ether before adding the methyl iodide. The product of the reaction proved to be a viscous, sticky liquid, which showed no signs of crystallisation after long standing over sulphuric acid in vacuo, and which could not be volatilised, even in vacuo, without decompositition. The substance dried over sulphuric acid in vacuo for several days gave somewhat too low a percentage of bromine.

0.3653 gram substance gave 0.3031 gram AgBr.

	Calculated for $C_4HBrO_4(CH_3)_2$.	Found.
Br	35.88	35.30

Diethyl Mucoxybromate, $C_4HBrO_4(C_2H_5)_2$.—This substance we attempted to prepare by the action of ethyl iodide diluted with dry ether upon the silver salt. We obtained a thick viscous product, which we were unable to purify, and which, after long standing over sulphuric acid in vacuo, proved to contain iodine, and gave too high a percentage of halogen.

I. 0.2288 gram substance gave 0.1911 gram AgBr.

II. 0.2328 gram substance gave 0.1920 gram AgBr.

	Calculated for $C_4HBrO_4(C_2H_5)_2$.	Found.	
		I.	II.
Br	31.82	35.56	35.10

The ether was decomposed by an excess of baric hydrate, the excess of baric hyrate precipitated by carbonic dioxide, and alcohol added to the filtrate solution. We obtained in this way a crystalline salt, which possessed ail the properties of baric mucoxybromate.

0.5875 gram of the air-dried salt gave 0.3720 gram $BaSO_4$.

	Calculated for $BaC_4HBrO_4.2H_2O$.	Found.
Ba	37.43	37.23

Monoethyl Mucoxybromate, $C_4H_2BrO_4.C_2H_5$.—If ordinary ether is used instead of anhydrous ether in the preparation of the ethyl ether, the acid ether is obtained. We added the dry silver salt slowly to an excess of ethyl iodide, and after the first reaction was over, warmed for a short time on the water-bath. The product was then extracted with ordinary ether, and the ethereal extract allowed to evaporate spontaneously. The syrupy residue thus obtained gradually yielded an abundance of clear prisms with oblique truncations, which were pressed out and recrystallised from boiling benzol.

0.2068 gram of substance dried over H_2SO_4 gave 0.1762 gram AgBr.

	Calculated for $C_4H_2BrO_4.C_2H_5$.	Found.
Br	35.88	36.25

The monoethyl mucoxybromate dissolves quite readily in water, its solution has a strongly acid reaction, and gives with ferric chloride an intense red coloration. It dissolves readily in alcohol, ether, chloroform, or hot benzol, more sparingly in ligroin or carbonic disulphide. The melting point of the substance repeatedly recrystallised from benzol was found to be 88°–89°.

Decomposition in Alkaline Solution.

The instability of mucoxybromic acid and its salts in aqueous solution led us to study the reaction more closely, with the hope that the products of this decomposition might throw light upon the constitution of the acid. When a solution of the barium salt is heated to boiling, it soon acquires an acid reaction, and before long grows turbid, with the separation of acid baric oxalate. The reaction then appears to progress slowly, and even after long boiling the decomposition is incomplete. In an alkaline solution, however, complete decomposition is readily effected. Baric hydrate appears to have no action upon mucoxybromic acid in the cold. After standing for days the solution is still clear, and contains no baric bromide. On heating, baric oxalate and baric carbonate are soon thrown down, and in solution may then be found baric bromide and baric formiate. The barium salts which were precipitated on boiling were collected on a filter, and the presence of oxalic and carbonic acids proved by qualitative tests. The oxalic acid was then converted into the calcium salt, and its identity further established by analysis.

0.3141 gram of the salt dried at 100° gave 0.2883 gram $CaSO_4$.

Calculated for $CaC_2O_4.H_2O$.	Found.
27.39	27.01

The alkaline solution filtered from the precipitated baric oxalate and carbonate was freed from the excess of baric hydrate by carbonic dioxide, and concentrated by evaporation on the water-bath. It gave with argentic nitrate a heavy precipitate of argentic bromide, and the filtered solution, containing an exces of argentic nitrate, deposited metallic silver on heating. After removing the barium with dilute sulphuric acid, the solution yielded an acid distillate, from which plumbic formiate was obtained by neutral-ising with plumbic carbonate.

0.2498 gram of the salt dried over H_2SO_4 gave 0.2542 gram $PbSO_4$.

Calculated for $Pb.(CHO_2)_2$.	Found.
69.69	69.50

Beside baric formiate and baric bromide the aqueous solution contained, in small but not insignificant quantity, an amorphous gummy barium salt, whose nature we have been unable to deter-mine, since all our attempts to convert it into a compound fit for analysis have proved unsuccessful. The formation of this gummy barium salt, together with the fact that quantitative determinations of the amounts of carbonic and oxalic acid formed in the reaction showed no simple ratio between the two, leaves little doubt that the reaction is essentially complex in its nature. When an aqueous solution of baric mucoxybromate is boiled with the addition of baric carbonate, the products of the decomposition appear to be the same. The action of water upon the free acid, which is doubtless similar, we have not yet studied in detail.

Action of Bromine in Aqueous Solution.

By the action of most of the ordinary oxidising agents upon mucoxybromic acid or its salts, we were unable to obtain any definite oxidation products except oxalic acid. Bromine water, however, gave us more satisfactory results. On adding bromine slowly to an aqueous solution of the acid, the color of the bromine rapidly disappeared, oxalic acid was formed, and at the same time a well-defined product containing bromine could be isolated. We found that the same reaction ensued, and apparently rather more

neatly, when the barium salt was taken instead of the free acid. Two molecules of bromine were therefore added to a dilute solution of the barium salt. After standing for several hours, the color of the bromine had completely disappeared, and crystals of acid baric oxalate had separated in abundance. The strongly acid solution was then neutralised with calcic carbonate, filtered, and extracted with ether. The ether left, on evaporation, a syrupy residue, which gradually deposited well-formed oblique prisms, which melted at 51°–52°. The melting point of the substance, its characteristic crystalline form, and its reactions with alkalies and argentic nitrate, left little doubt that it was bromal hydrate, although the percentage of bromine which it gave on analysis was somewhat too low.

0.1351 gram substance gave 0.2534 gram AgBr.

	Calculated for $C_2Br_3H_3O_2$.	Found.
Br	80.26	79.84

We found that the purification of this substance by recrystallisation was attended with so great loss that we could hardly draw any definite conclusion as to the composition of the main product from analyses of the small purified residue, and we therefore determined to examine the products formed from it by the action of alkalies. Instead of extracting with ether the solution neutralised with calcic carbonate, we added to it a slight excess of potassic hydrate, and distilled, after neutralising the slightly alkaline solution with hydrochloric acid. In this way we obtained a colorless, heavy oil, which was easily recognised as bromoform. After drying over fused calcic chloride, it boiled at 147°–150°, under a pressure of 748 mm. Its identity was further established by analysis.

I. 0.1739 gram substance gave 0.3893 gram AgBr.

II. 0.2202 gram substance gave 0.4940 gram AgBr.

	Calculated for $CHBr_3$.	Found. I.	II.
Br	94.86	95.28	95.48

The weight of bromoform thus obtained amounted to between sixty and seventy per cent. of that required by the assumption that each molecule of the acid yielded one molecule of bromal.

The residue left after distilling off the bromoform was then acidified and distilled with steam. The acid distillate contained formic

acid, as was shown by the ordinary qualitative tests and by the analysis of the lead salt prepared from it.

0.3193 gram of the salt dried at 100° gave 0.3256 gram PbSO₄.

	Calculated for Pb.(CHO₂)₂.	Found.
Pb	69.69	69.66

One of the products of the reaction was therefore bromal. In the insoluble residue removed by filtration after neutralising with calcic carbonate was found oxalic acid in abundance, which was identified by qualitative reactions and by the analysis of its calcium salt.

0.3779 gram of the salt dried at 100° gave 0.3490 gram CaSO₄.

	Calculated for CaC₂O₄.H₂O.	Found.
Ca	27.39	27.16

The decomposition of mucoxybromic acid by aqueous bromine may therefore be expressed by the equation

$$C_4H_3BrO_4 + 2Br_2 + H_2O = C_2HBr_3O + H_2C_2O_4 + 2HBr.$$

Although phenylhydrazine readily reacts upon mucoxybromic acid, even in dilute solution, the flocculent product formed rapidly turns brown, and we have not succeeded in obtaining it in a form fit for analysis. Hydroxylamine also yielded no more satisfactory results, although we tried the reaction under a variety of conditions. On the other hand, the primary aromatic amines in neutral or acid solutions gave beautifully crystalline products with the greatest readiness. Aniline, parabromaniline, para- and metanitraniline, ortho- and paratoluidine, all yielded similar products, but we have thus far studied in detail the aniline compound alone. Urea likewise gives a crystalline condensation product which has not yet been further investigated.

Anilmucoxybromic Acid.

When aniline chloride is added to a dilute solution of mucoxybromic acid, the solution soon becomes yellow, and after a short time solidifies, with the separation of finely felted, light yellow needles. A moderate excess of free hydrochloric acid in no way interferes with the formation of the product, so that it may be most conveniently prepared by dissolving baric mucoxybromate in a slight excess of dilute hydrochloric acid, and adding a mole-

cule of aniline dissolved in hydrochloric acid. The product was recrystallised from hot water, dried over sulphuric acid, and proved then to be anilmucoxybromic acid, formed according to the equation

$$C_4H_3BrO_4 + C_6H_5NH_2 = C_4H_3BrO_3.C_6H_5N + H_2O.$$

I. 0.2775 gram substance gave 0.4540 gram CO_2 and 0.0790 gram H_2O.

II. 0.2602 gram substance gave 0.1810 gram AgBr.

III. 0.2526 gram substance gave 0.1764 gram AgBr.

IV. 0.5563 gram substance gave 25.2 cc. of moist nitrogen at 19° and under a pressure of 748 mm.

	Calculated for $C_{10}H_8BrNO_3$.	I.	II.	III.	IV.
C	44.44	44.62			
H	2.96	3.16			
Br	29.63	...	29.61	29.73	
N	5.18	...	...	...	5.21

The air-dried acid apparently contained one molecule of water, which it lost rapidly over sulphuric acid or when heated to 70°. At 100° a slow decomposition appeared to take place. The loss of crystal water was accompanied by a change of color to brilliant yellow.

I. 0.5579 gram of air-dried substance lost, at 62°–65°, 0.0362 gram H_2O.

II. 0.9504 gram of air-dried substance lost, at 70°, 0.0630 gram H_2O.

III. 1.0217 gram of air-dried substance lost over sulphuric acid 0.0786 gram H_2O.

	Calculated for $C_{10}H_8BrNO_3.H_2O$.	I.	II.	III.
H_2O	6.25	6.49	6.63	7.69

Anilmucoxybromic acid crystallises from water in fine pale yellow needles, which are sparingly soluble in cold water, more readily in hot. On long heating of the aqueous solution decomposition sets in. The acid dissolves readily in alcohol, ether, or in hot chloroform or benzol; in ligroin or carbonic disulphide it is sparingly soluble. From chloroform it crystallises in small compact oblique prisms, which melt, with decomposition, at 131°–132°. The acid dissolves readily in solutions of the alkaline carbonates, and is re-precipitated unchanged on the addition of acids. With the salts

of the heavy metals it gives brilliant yellow insoluble salts, and
with ferric chloride it yields a deep brown precipitate. On heating
with acids or alkalies, aniline is formed. On titration with baric
hydrate two molecules of the acid were found to be neutralised by
one molecule of baric hydrate, but salts containing two atoms of
silver and potassium could also be prepared.

Monobaric Anilmucoxybromate, $Ba(C_{10}H_7BrNO_3)_2 \frac{1}{2} H_2O$.—By
the action of baric carbonate upon the acid suspended in water, a
salt is formed which is somewhat sparingly soluble in hot or cold
water. On evaporation of the solution a portion of the salt sepa-
rates in yellow needles, but decomposition soon ensues. On the
addition of baric acetate to the acid neutralised with ammonic
hydrate, an amorphous flocculent precipitate was thrown down,
which dissolved on heating, and immediately in its place there
appeared a highly crystalline bright yellow precipitate. As the
solution cooled, still more of the salt separated in felted needles.
The air-dried salt apparently contained a half-molecule of crystal
water, which it lost at 100°.

0.5802 gram of the air-dried salt lost, at 100°, 0.0075 gram H_2O.

	Calculated for $Ba.(C_{10}H_7BrNO_3)_2 \frac{1}{2} H_2O$.	Found.
H_2O	1.32	1.25

0.5755 gram of this salt dried at 100° gave 0.1970 gram $BaSO_4$.

	Calculated for $Ba.(C_{10}H_7BrNO_3)_2$.	Found.
Ba	20.30	20.12

Diargentic Anilmucoxybromate, $Ag_2C_{10}H_6BrNO_3$. — When
argentic nitrate was added to an aqueous solution of the free acid,
a pale yellow gelatinous precipitate was thrown down, which
apparently contained one atom of silver. If, however, the acid
was dissolved in two equivalents of ammonic hydrate, and the
solution was then added to an excess of argentic nitrate, a volumi-
nous bright orange-yellow precipitate was thrown down, which on
standing became dense and semi-crystalline, and contained two
atoms of silver. When warmed with an excess of argentic nitrate
in a feebly ammoniacal solution, no immediate reduction took
place.

0.4275 gram of the salt dried over H_2SO_4 gave 0.3290 gram
AgBr.

	Calculated for $Ag_2C_{10}H_6BrNO_3$.	Found.
Ag	44.64	44.21

Dipotassic Anilmucoxybromate, $K_2C_{10}H_6BrNO_3$.—On the addition of an alcoholic solution of potassic hydrate to a solution of the acid in anhydrous ether, a pale yellow salt was thrown down, which was well washed with anhydrous ether, and dried in vacuo over sulphuric acid and solid sodic hydrate.

0.3556 gram of the salt gave 0.1805 gram K_2SO_4.

Calculated for $K_2C_{10}H_6BrNO_3$.   Found.
22.58   22.79

While anilmucoxybromic acid forms by preference monobasic salts, it is evidently capable of exchanging two of its hydrogen atoms for metals.

Phenylhydrazine Anilmucoxybromate, $C_{10}H_8BrNO_3.C_6H_5N_2$. H_2O.—When phenylhydrazine hydrochlorate is added to anilmucoxybromic acid dissolved in a dilute solution of sodic acetate, a colorless crystalline precipitate soon separates, which, after washing with cold water, becomes somewhat discolored on drying. The compound is but sparingly soluble in cold water, more readily in hot, but it cannot be recrystallised from hot water without decomposition. It is readily soluble in alcohol, but nearly insoluble in ether. It is readily decomposed in the cold by dilute hydrochloric acid, or by a dilute solution of sodic carbonate, with the formation of phenylhydrazine. This behavior showed the substance to be a simple salt of phenylhydrazine, and analysis also failed to show the elimination of water.

0.3708 gram of the air-dried substance gave 36.5 cc. of moist nitrogen at 25° under a pressure of 726 mm.

Calculated for $C_{16}H_{16}BrN_3O_3.H_2O$.   Found.
N   10.60   10.77

Mucoxychloric Acid.

W. Z. Bennett[1] and one of us several years ago studied the action of baric hydrate upon mucochloric acid. It was found that the acid was decomposed by a large excess of baric hydrate, and that α,β dichloracrylic and formic acids were formed in nearly theoretical quantities. When the baric hydrate is carefully added, so that the solution is at no time very strongly alkaline, the reaction follows an entirely different course, and mucoxychloric acid is found in abundance. Since the α,β dichloracrylic acid had already

[1] Proceedings American Academy **16**, 206.

been shown to be more stable than the corresponding dibrom-acrylic acid, we were led to study mucoxychloric acid more in detail, with the hope that its derivatives would also prove more stable and more manageable than those of mucoxybromic acid. In the preparation of mucoxychloric acid we followed precisely the same method which we had found advantageous with the bromine compound. Mucochloric acid[1] was suspended in 35 times its weight of water, and, after cooling well with ice, the theoretical quantity of finely powdered baric hydrate was slowly added, taking care to avoid at any time a large excess. After the requisite amount of baric hydrate had been added, we allowed the solution to stand over night, and removed the slight excess of baric hydrate, which was then usually found present, by means of carbonic dioxide. The filtered solution gave, when mixed with an equal volume of alcohol, a voluminous highly crystalline precipitate of baric mucoxychlorate, which could be purified by reprecipitation from aqueous solution by alcohol. In this way we have obtained 73 per cent. of the theoretical amount of barium salt demanded by the equation

$$2C_4H_2Cl_2O_3 + 3BaO_2H_2 = 2BaC_4HClO_4 + BaCl_2 + 4H_2O.$$

The mother liquors contain, beside baric chloride, baric $a\beta$ dichloracrylate, which may be obtained without difficulty by the evaporation of the solution. Although ether extracts the acid

[1] Although W. Z. Bennett and I had succeeded in obtaining a fairly satisfactory yield of mucochloric acid, the method which we used was troublesome and tedious in the extreme when large quantities of material were involved, and necessitated the prolonged treatment of large quantities of liquid at o° with chlorine gas. The slightest want of care also frequently diminished the yield most seriously. I therefore made many fruitless attempts to find some more advantageous method for its preparation. I at last hit upon an extremely convenient and simple method, which allows the preparation of any quantity of mucochloric acid desired in the course of a few hours. The yield is also quite satisfactory, and falls not far short of that which is attainable by the old method. Pyromucic acid is suspended in 14½ times its weight of common strong hydrochloric acid (sp. gr. 1.16), and somewhat more than four molecules of finely powdered manganic dioxide are then gradually added. At first the mixture is kept cold (ice cooling is unnecessary). The temperature is then allowed to rise, and finally the solution is heated and boiled gently for twenty minutes. Since it is difficult to filter the hot strongly acid liquid from the impurities contained in the manganic dioxide, the solution is allowed to cool, and the mucochloric acid which separates collected upon a filter of coarse cloth. It is then dissolved in hot water, and the filtered solution concentrated by evaporation if necessary. From 100 grams of pyromucic acid suspended in 1250 cc. of ordinary hydrochloric acid and 380 grams of manganese dioxide (83 per cent. MnO_2), 50 grams of pure mucochloric acid are readily obtained, and the mother liquors yield 2-3 grams of a somewhat dark-colored acid. Bennett and I obtained by the much more laborious method, as the result of many separate operations, 129 grams of mucochloric acid from 202 grams pyromucic acid. This method accordingly yields in a short time about 83 per cent. of the amount attainable by the more tedious method. —H. B. H.

from aqueous solution, it does not take it up very readily, and we have found it more advantageous to precipitate the barium salt exactly with dilute sulphuric acid, and evaporate the aqueous solution thus obtained in vacuo over sulphuric acid. The acid may readily be recrystallised with care from a little warm water. For analysis the acid was dried over sulphuric acid.

I. 0.2925 gram substance gave 0.3420 gram CO_2 and 0.0615 gram H_2O.

II. 0.1990 gram substance gave 0.1915 gram AgCl.

III. 0.2000 gram substance gave 0.1918 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	I.	Found. II.	III.
C	31.89	31.88		
H	1.99	2.33		
Cl	23.59	...	23.79	23.71

Mucoxychloric acid is readily soluble in water, alcohol, or ether, and almost insoluble in chloroform, benzol, ligroin, or carbonic disulphide. From water it crystallises in stout prisms with beveled ends, which melt at 114°–115°. With ferric chloride it gives, even in extremely dilute solutions, a deep garnet-red coloration. With argentic nitrate it gives an immediate crystalline precipitate of the silver salt. Although more stable than mucoxybromic acid, it is soon decomposed by warming its aqueous solution.

Baric Mucoxychlorate, $BaC_4HClO_4.2H_2O$.—The preparation of the barium salt has already been described. It is sparingly soluble in cold water, more readily in hot, and is nearly insoluble in dilute alcohol. Although it is decomposed by heating its aqueous solution, the decomposition is not particularly rapid, and small quantities of the salt may be recrystallised from hot water with little difficulty. It crystallises then in fine clustered needles, and is obtained in the same form by precipitating its aqueous solution with alcohol. In evaporating a cold aqueous solution in vacuo over sulphuric acid, the salt may be obtained in long lustrous prisms with perpendicular terminations. The salt crystallised from water, or precipitated by alcohol, when air-dried, loses over sulphuric acid somewhat more than one molecule of water, and has then the composition $BaC_4HClO_4.H_2O$.

I. 2.5352 grams of salt recrystallised from water and dried by exposure to the air lost over sulphuric acid 0.1706 gram H_2O.

II. 2.2127 grams of salt recrystallised from water and dried by exposure to the air lost over sulphuric acid 0.1480 gram H_2O.

III. 1.9160 grams of salt precipitated by alcohol and dried by exposure to the air lost over sulphuric acid 0.1288 gram H_2O.

IV. 1.5273 grams of salt precipitated by alcohol and dried by exposure to the air lost over sulphuric acid 0.1054 gram H_2O.

	Calculated for $BaC_4HClO_4.2HO_2$.	I.	Found. II.	III.	IV.
$1H_2O$	5.60	6.73	6.69	6.73	6.90

The salt dried over sulphuric acid contained a percentage of barium agreeing closely with that required by the formula $BaC_4HClO_4.H_2O$. It lost weight slowly at $100°-105°$, but only the compact salt crystallised from water could be brought to constant weight at this temperature without essential decomposition. The voluminous salt precipitated by alcohol after many weeks still lost in weight, contained baric chloride, and had become badly discolored.

I. 1.4644 grams of salt recrystallised from water and dried over sulphuric acid lost, at $100°-105°$, 0.0820 gram H_2O.

II. 1.4771 grams of salt recrystallised from water and dried over sulphuric acid lost, at $100°-105°$, 0.0827 gram H_2O.

III. 0.8947 gram of salt recrystallised from water and dried over sulphuric acid gave 0.6871 gram $BaSO_4$.

IV. 0.5865 gram of salt recrystallised from water and dried over sulphuric acid gave 0.4498 gram $BaSO_4$.

V. 0.3261 gram of salt precipitated by alcohol and dried over sulphuric acid gave 0.3266 gram $BaSO_4$.

	Calculated for $BaC_4HClO_4.H_2O$.	I.	II.	Found. III.	IV.	V.
H_2O	5.93	5.60	5.60			
Ba	45.14	...	...	45.16	45.08	45.06

Although the crystallised baric mucoxychlorate suffers no change when exposed to the air for a week or more, after months of exposure it loses in weight and the clear prismatic crystals become opaque. The salt is then more sparingly soluble in water, and crystallises in small oblique prisms. These same oblique crystals are also occasionally deposited together with the long rectangular prisms on evaporating in vacuo the aqueous solution of the salt originally obtained. An analysis showed that these oblique prisms contained a percentage of barium required by a salt crystallising with one molecule of water. Although the crystalline form appeared to be persistent, we were able to detect no

differences in the chemical behavior of the salt, or of the acid prepared from it, which would warrant the assumption that any radical change in its structure had taken place.

For analysis, the oblique prisms were well washed with cold water and dried by exposure to the air. The air-dried salt lost nothing over sulphuric acid, and lost weight but slowly at $100°$.

0.4076 gram of air-dried salt gave 0.3131 gram $BaSO_4$.

	Calculated for $BaC_4HClO_4.H_2O$.	Found.
Ba	45.14	45.15

Potassic Mucoxychlorate, $K_2C_4HClO_4$.—The potassium salt we prepared by decomposing the barium salt with potassic carbonate and evaporating the filtered solution in vacuo over sulphuric acid. The salt separated in small tabular crystals, which were recrystallised from warm water. The air-dried salt lost nothing when heated at $100°$.

I. 0.4344 gram of the salt gave 0.3334 gram K_2SO_4.

II. 0.4631 gram of the salt gave 0.3547 gram K_2SO_4.

	Calculated for $K_2C_4HClO_4$.	I.	II.
		Found.	
K	34.49	34.45	34.39

Argentic Mucoxychlorate, $Ag_2C_4HClO_4$.—The silver salt was made by precipitating a solution of argentic nitrate with a solution of the potassium salt. On heating, argentic chloride was rapidly formed. On warming with a little ammonic hydrate, immediate reduction ensued. From a solution of the free acid, argentic nitrate threw down the neutral salt (III).

I. 0.5024 gram of the salt dried over H_2SO_4 gave 0.3948 gram AgCl.

II. 0.4125 gram of the salt dried over H_2SO_4 gave 0.3240 gram AgCl.

III. 0.3704 gram of the salt dried over H_2SO_4 gave 0.2891 gram AgCl.

	Calculated for $Ag_2C_4HClO_4$.	I.	II.	III.
		Found.		
Ag	59.27	59.17	59.13	58.76

Diethyl Mucoxychlorate, $C_4HClO_4(C_2H_5)_2$.—Finely powdered argentic mucoxychlorate, which had been well dried over sulphuric acid, was gradually thrown into an excess of ethyl iodide. The heat evolved by the reaction was so great that the boiling point of the ethyl iodide was soon reached, and the decomposition was

afterward completed by heating for a short time on the water-bath. The product of the reaction was then extracted by dry chloroform, the chloroform distilled off under diminished pressure, and the viscous residue placed over sulphuric acid in vacuo. After long standing in vacuo the product showed no signs of crystallisation, but proved to contain a percentage of chlorine which agreed tolerably well with that required by the diethyl ether.

0.2314 gram substance gave 0.1553 gram AgCl.

	Calculated for $C_4HClO_4(C_2H_5)_2$.	Found.
Cl	17.19	16.59

Monoethyl Mucoxychlorate, $C_4H_2ClO_4.\dot{C}_2H_5.$—When the viscous diethyl ether just described was allowed to stand exposed to the air, or when it was mixed with a small quantity of water, it rapidly acquired an acid reaction, and gradually deposited well-formed crystals of the monoethyl ether. The latter could also readily be prepared by extracting with ordinary aqueous ether the product formed by the action of ethyl iodide upon the silver salt, and allowing the ethereal solution to evaporate spontaneously. The crystals which separated were thoroughly pressed and recrystallised from boiling benzol.

I. 0.2337 gram substance gave 0.3445 gram CO_2 and 0.0870 gram H_2O.

II. 0.2659 gram substance gave 0.2147 gram AgCl.

III. 0.2572 gram substance gave 0.2080 gram AgCl.

	Calculated for $C_4H_2ClO_4.C_2H_5.$	I.	Found. II.	III.
C	40.33	40.20		
H	3.92	4.13		
Cl	19.89	...	19.95	20.00

Monoethyl mucoxychlorate crystallises in clustered, obliquely truncated prisms, which melt at 94°–95°, and sublime unchanged at higher temperature. It dissolves readily in water, alcohol, ether, or chloroform, quite readily in boiling benzol, more sparingly in cold, and but sparingly in ligroin. Its aqueous solution is strongly acid to litmus, dissolves carbonates with effervescence, and gives a deep red coloration with ferric chloride. When baric hydrate is slowly added to the aqueous solution, a yellow color is developed, and products formed which we have not yet more fully studied. If, however, the ether is dissolved in an excess of baric hydrate, it is saponified and baric mucoxychlorate formed. The alkaline

solution was precipitated with carbonic dioxide, and alcohol added to the filtered solution. The crystalline salt which separated was dissolved in cold water, and the solution evaporated over sulphuric acid in vacuo.

0.7070 gram of air-dried salt lost over sulphuric acid 0.0482 gram H_2O.

	Calculated for $BaC_4HClO_4.2H_2O$.	Found.
$1H_2O$	5.60	6.82

0.6588 gram of the salt dried over H_2SO_4 lost, at 100°, 0.0385 gram H_2O.

	Calculated for $BaC_4HCl.H_2O$.	Found.
H_2O	5.93	5.85

0.6203 gram of the salt dried at 100° gave 0.3535 gram $BaSO_4$.

	Calculated for BaC_4HClO_4.	Found.
Ba	47.98	47.85

Decomposition in Alkaline Solution.

The instability of mucoxychloric acid and its salts when heated in aqueous solution has already been mentioned. We have, however, as yet studied more closely only the reaction which takes place when baric mucoxychlorate is heated with an excess of baric hydrate. The solution soon grows turbid on boiling, and throws down baric oxalate and baric carbonate, while the solution then contains baric chloride and formiate. The insoluble salts were collected upon a filter, and the presence of carbonic and oxalic acids established by qualitative tests. The presence of oxalic acid was still further confirmed by an analysis of the calcium salt.

0.1740 gram of the salt dried at 100° gave 0.1608 gram $CaSO_4$.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.39	27.17

The aqueous solution filtered from the insoluble salts was freed from the excess of baric hydrate by means of carbonic dioxide. It gave then with argentic nitrate an abundant precipitate of argentic chloride, and blackened when heated with an excess of argentic nitrate. The barium was removed by dilute sulphuric acid, and the filtered solution distilled. The acid distillate when neutralised with plumbic carbonate yielded plumbic formiate in characteristic form.

0.3244 gram of the salt dried at 100° gave 0.3327 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	70.06

As was the case with the corresponding decomposition of mucoxybromic acid, quantitative determinations of the amounts of oxalic and carbonic acid formed in the reaction showed no simple relation between the two, and at the same time products were formed in small but significant amounts, whose nature we have as yet been unable to determine.

Action of Bromine in Aqueous Solution.

Bromine acts readily upon an aqueous solution of mucoxychloric acid, and forms products strictly analogous to those formed from mucoxybromic acid under the same conditions. Since the chlorobromal hydrate proved to be even less manageable than the bromal hydrate, we thought it best to determine its presence, as before, from its decomposition products. Since the reaction seemed to be quite as neat with the salts as with the free acid, we added to a diluted aqueous solution of the barium salt two molecules of bromine, and allowed the mixture to stand at ordinary temperatures until the color of the bromine had completely disappeared. We then neutralised the strongly acid solution with calcic carbonate in the cold, and filtered. The insoluble residue thus obtained contained oxalic acid in abundance, and we were unable to detect in it any other organic constituent. The oxalic acid was converted into its calcium salt and analysed.

0.3489 gram of the salt dried at 100° gave 0.3212 gram $CaSO_4$.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.39	27.08

To the clear aqueous solution we added a slight excess of potassic hydrate, neutralised after a short time with hydrochloric acid, and distilled the neutral solution with steam. We obtained in this way a colorless heavy oil, which, when dried with calcic chloride, boiled without decomposition at 119°–120° under a pressure of 748 mm.[1] Analysis showed it to be dibromchlormethan.

I. 0.1545 gram substance gave 0.3855 gram $AgCl + AgBr$.

II. 0.1418 gram substance gave 0.3536 gram $AgCl + AgBr$.

	Calculated for $CHClBr_2$.	Found. I.	II.
Cl + Br	93.74	93.91	93.85

The weight of dibromchlormethan thus obtained was about sixty per cent. of the theoretical amount.

---

[1] According to O. Jacobsen and R. Neumeister (Ber. d. deutsch. chem. Gesellsch. **15**, 601), chlorobromoform boils between 123° and 125°, with slight decomposition.

The residue left after distillation was acidified, and again distilled with steam. The acid distillate thus obtained was neutralised with plumbic carbonate, and yielded upon evaporation plumbic formiate.

0.3936 gram of the salt dried at 100° gave 0.4003 gram $PbSO_4$.

	Calculated for $Pb.(CHO_2)_2$.	Found.
Pb	69.69	69.47

The decomposition of mucoxychloric acid by aqueous bromine may therefore be expressed by the equation

$$C_4H_3ClO_4 + 2Br_2 + H_2O = H_2C_2O_4 + CClBr_2CHO + 2HBr.$$
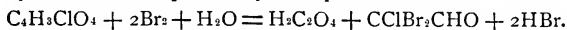
Anilmucoxychloric Acid.

Mucoxychloric acid, like mucoxybromic acid, readily gives with phenylhydrazine a condensation product. It has, however, little stability, and we have therefore not studied it more closely. With aniline, however, it gives even in dilute acid solutions a beautifully crystalline product. For its preparation we added one molecule of aniline hydrochlorate to a solution of the barium salt in a slight excess of dilute hydrochloric acid. The solution soon turned yellow, and after standing for a short time solidified with the separation of pale yellow finely felted needles. At low temperatures the crystals formed were often nearly colorless. When recrystallised from hot water and dried over sulphuric acid, the substance was shown by analysis to be anilmucoxychloric acid formed according to the equation

$$C_4H_3ClO_4 + C_6H_5NH_2 = C_4H_3ClO_3.NC_6H_5 + H_2O.$$
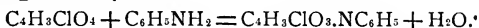
I. 0.2146 gram substance gave 0.4170 gram CO_2 and 0.0791 gram H_2O.

II. 0.1797 gram substance gave 0.1142 gram AgCl.

III. 0.1865 gram substance gave 0.1186 gram AgCl.

IV. 1.0389 gram substance gave 60.6 cc. moist nitrogen at 23° and under a pressure of 746 mm.

	Calculated for $C_{10}H_8ClNO_3$.	I.	II.	Found. III.	IV.
C	53.21	52.99			
H	3.54	4.10			
Cl	15.74	...	15.71	15.72	
N	6.21	...	...	...	6.60

The air-dried acid apparently contains one molecule of water of crystallisation, which it loses readily over sulphuric acid or when

heated to 100°. With the loss of water the pale yellow or almost colorless needles become brilliant yellow.

I. 0.7579 gram of air-dried acid lost, at 100°, 0.0597 gram H_2O.

II. 0.9022 gram of air-dried acid lost, at 100°, 0.0702 gram H_2O.

III. 0.5646 gram of air-dried acid lost over H_2SO_4 0.0460 gram H_2O.

	Calculated for $C_{10}H_8ClNO_3$.	I.	Found. II.	III.
H_2O	7.39	7.88	7.78	8.15

Anilmucoxychloric acid is sparingly soluble in cold water, more readily in hot, and appears to suffer slow decomposition when its aqueous solution is boiled. It dissolves readily in alcohol or ether, sparingly in cold benzol or chloroform, more freely on heating. In ligroin or carbonic disulphide it is nearly insoluble. From chloroform it crystallises in small compact oblique prisms, which melt with decomposition at 145°–147°. The acid dissolves readily in solutions of the alkaline carbonates, and is reprecipitated unchanged by the addition of acids. In heating with acids or alkalies aniline is formed. An aqueous solution of the free acids gives deep yellow precipitates with salts of most of the heavy metals. With ferric chloride it gives a deep brown precipitate. It forms by preference monobasic salts, but we have prepared also dibasic salts.

Baric Anilmucoxychlorate, $Ba(C_{10}H_7ClNO_3)_2\frac{1}{2}H_2O$.—If baric carbonate is added to anilmucoxychloric acid suspended in cold water, carbonic dioxide is disengaged, and a barium salt readily soluble in water is formed. If the concentrated filtered solution is then heated nearly to boiling, it soon deposits abundant bright yellow clustered needles, which increase somewhat in quantity as the solution cools. The air-dried salt lost slightly in weight at 100°. This loss corresponded to about one half-molecule of crystal water; it is possible, however, that it was hygroscopic moisture alone.

I. 0.2819 gram of the air-dried salt lost, at 100°, 0.0052 gram H_2O.

II. 0.9735 gram of the air-dried salt lost, at 100°, 0.0196 gram H_2O.

	Calculated for $Ba(C_{10}H_7ClNO_3)_2\frac{1}{2}H_2O$.	I.	Found. II.
H_2O	1.51	1.85	2.01

I. 0.2767 gram of the salt dried at 100° gave 0.1102 gram $BaSO_4$.

II. 0.3918 gram of the salt dried at 100° gave 0.1561 gram BaSO₄.

	Calculated for Ba(C₁₀H₇ClNO₉)₂.	Found.	
		I.	II.
Ba	23.37	23.42	23.42

Diargentic Anilmucoxychlorate, $Ag_2C_{10}H_6ClNO_3$.—When argentic nitrate is added to a cold aqueous solution of anilmucoxychloric acid, a pale yellow gelatinous precipitate is formed, which is hard to wash and prepare for analysis, and doubtless contains one atom of silver. If, however, the acid is dissolved in two equivalents of dilute ammonic hydrate, and this solution poured into an excess of argentic nitrate, a bright orange-yellow flocculent precipitate is thrown down, which becomes more compact on standing, and contains two atoms of silver. This salt showed but slight discoloration when warmed for some time with an excess of argentic nitrate in a feebly ammoniacal solution.

0.5431 gram of the salt dried over H_2SO_4 gave 0.3516 gram AgCl.

	Calculated for Ag₂C₁₀H₆ClNO₃.	Found.
Ag	49.15	48.73

Dipotassic Anilmucoxychlorate, $K_2C_{10}H_6ClNO_3$.—When an alcoholic solution of potassic hydrate was added, in slight excess, to a solution of anilmucoxychloric acid in dry ether, a pale yellow salt was precipitated, which when dried in vacuo over sulphuric acid and powdered sodic hydrate proved to contain two atoms of potassium.

0.6070 gram of the salt gave 0.3579 gram K_2SO_4.

	Calculated for K₂C₁₀H₆ClNO₃.	Found.
K	25.92	26.47

Phenylhydrazine Anilmucoxychlorate, $C_{10}H_8ClNO_3.C_6H_8N_2.$ H_2O.—When phenylhydrazine hydrochlorate is added to anilmucoxychloric acid dissolved in a dilute solution of sodic acetate, a white crystalline substance soon separates, which becomes somewhat discolored on drying. It is sparingly soluble in cold water, readily soluble in alcohol, but insoluble in ether. It is decomposed in the cold by dilute hydrochloric acid, or by a dilute solution of sodic carbonate, with the formation of phenylhydrazine. This behavior shows that it is simply a salt of phenylhydrazine rather than a characteristic condensation product. The substance was well washed with cold water and dried over sulphuric acid.

I. 0.3000 gram substance gave 0.1189 gram AgCl.

II. 0.3218 gram substance gave 34 cc. of moist nitrogen at 18°
and under a pressure of 748 mm.

III. 0.2248 gram substance gave 23.5 cc. moist nitrogen at 20°
and under a pressure of 741 mm.

	Calculated for $C_{16}H_{16}ClN_3O_3.H_2O$.	I.	Found. II.	III.
Cl	9.98	9.80		
N	11.81	...	12.20	11.87

THEORETICAL CONSIDERATIONS.

Although the facts which we have observed are in certain
respects difficult of interpretation, it seems to us that, on the whole,
they warrant tolerably definite conclusions as to the constitution of
mucoxybromic and mucoxychloric acids. We may safely assume
that mucobromic and mucochloric acids are to be represented by
the formulæ[1]

$$
\begin{array}{cc}
C\!\!<^H_O & C\!\!<^H_O \\
| & | \\
CBr & CCl \\
\| & \| \\
CBr & CCl \\
| & | \\
COOH & COOH.
\end{array}
$$
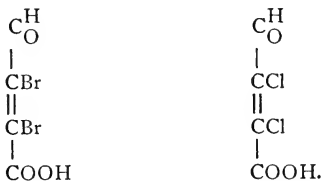
It is evident that the carboxyl group is not affected by the reac-
tion in question, and, furthermore, that the aldehyde group is also
still contained in the mucoxybromic and mucoxychloric acids.
The latter fact is sufficiently proved by the behavior of the two
acids with argentic nitrate, by the ready formation of condensation
products with aniline, and, lastly, by the appearance of substituted
aldehydes among the products formed from them by the action of
aqueous bromine. The two central carbon atoms are therefore
alone concerned in the transformation of mucobromic and muco-
chloric acids into the corresponding oxy-acids ; and the first steps
at least in this change must be the replacement of one of the
halogen atoms by hydroxyl.

Since potassic phenylate acts upon mucobromic acid with the
formation of mucophenoxybromic acid, whose constitution has
been shown to be[2]

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[1] Proceedings American Academy **16**, 218; **17**, 150.

[2] This Journal **6**, 194; and Proceedings American Academy **19**, 268.

$$C_O^H$$
$$|$$
$$CBr$$
$$||$$
$$C-O-C_6H_5$$
$$|$$
$$COOH,$$
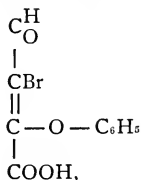
it could safely be assumed that in the analogous reaction with baric hydrate the a-halogen atom would also be first replaced. The formation of dibromchlor aldehyde,

$$C_O^H$$
$$|$$
$$C_{Br_2}^{Cl},$$

by the action of bromine upon mucoxychloric acid, proves that this assumption is correct, since the β-chlorine atom has here retained its place. It follows, therefore, that the mucoxybromic and mucoxychloric acids are either hydroxyl acids formed by the replacement of the a-halogen atoms by hydroxyl,

$$C_O^H \qquad\qquad C_O^H$$
$$| \qquad\qquad\qquad |$$
$$CBr \qquad\qquad CCl$$
$$|| \qquad\qquad\qquad ||$$
$$C-OH \qquad\qquad C-OH$$
$$| \qquad\qquad\qquad |$$
$$COOH \qquad\qquad COOH,$$
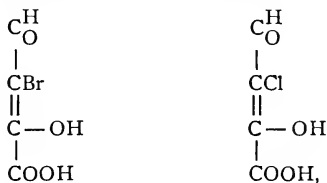
or that they are the ketone acids,

$$C_O^H \qquad\qquad C_O^H$$
$$| \qquad\qquad\qquad |$$
$$C_H^{Br} \qquad\qquad C_H^{Cl}$$
$$| \qquad\qquad\qquad |$$
$$CO \qquad\qquad CO$$
$$| \qquad\qquad\qquad |$$
$$COOH \qquad\qquad COOH,$$
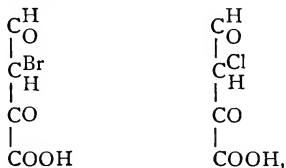
formed from them by the ordinarily observed molecular rearrangement.

While a satisfactory explanation of the persistent dibasic character

of the two acids can hardly be found in these formulæ, the formation of dibasic salts from either cannot be pronounced impossible, and no definite argument in favor of either formula can be based upon this behavior.

The ready and complete saponification of the ether of the two acids with the formation of the original dibasic metallic salts seems on the other hand an insurmountable objection to the ketone formula. The diethyl ethers of the ketone acids,

$$
\begin{array}{ll}
C\!\!\begin{array}{l}H\\O\end{array} & \qquad C\!\!\begin{array}{l}H\\O\end{array} \\
| & \qquad | \\
C\!\!\begin{array}{l}Br\\ \diagdown C_2H_5\end{array} & \qquad C\!\!\begin{array}{l}Cl\\ \diagdown C_2H_5\end{array} \\
| & \qquad | \\
CO & \qquad CO \\
| & \qquad | \\
COOC_2H_5 & \qquad CO.OC_2H_5,
\end{array}
$$
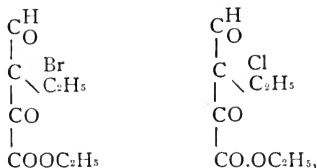
must of necessity yield upon saponification homologous monobasic acids,

$$
\begin{array}{ll}
C\!\!\begin{array}{l}H\\O\end{array} & \qquad C\!\!\begin{array}{l}H\\O\end{array} \\
| & \qquad | \\
C\!\!\begin{array}{l}Br\\ \diagdown C_2H_5\end{array} & \qquad C\!\!\begin{array}{l}Cl\\ \diagdown C_2H_5\end{array} \\
| & \qquad | \\
CO & \qquad CO \\
| & \qquad | \\
COOH & \qquad COOH,
\end{array}
$$
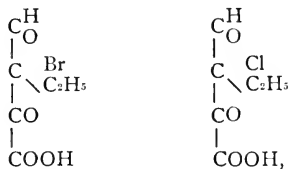
unless indeed a complete destruction of the molecule ensues.

We are therefore unable to resist the conclusion that mucoxybromic and mucoxychloric acids contain hydroxyl—that they are in fact phenol acids of the paraffine series, in which the hydroxyl has strongly marked acid properties on account of its peculiar environment.

The anomalous removal of the ethyl groups from the ethers,

$$
\begin{array}{ll}
C\!\!\begin{array}{l}H\\O\end{array} & \qquad C\!\!\begin{array}{l}H\\O\end{array} \\
| & \qquad | \\
CBr & \qquad CCl \\
| & \qquad | \\
C\!-\!O.C_2H_5 & \qquad C\!-\!O.C_2H_5 \\
| & \qquad | \\
COOC_2H_5 & \qquad COOC_2H_5,
\end{array}
$$
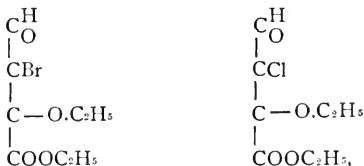
by saponification with baric hydrate, seems to us to be conditioned

by the strongly acid character of this hydroxyl, a character which is usually wholly wanting. To the acid ethers formed by the action of water in the cold must be assigned the formulæ

$$
\begin{array}{ll}
C_O^H & C_O^H \\
| & | \\
CBr & CCl \\
| & | \\
C-O-C_2H_5 & C-O-C_2H_5 \\
| & | \\
COOH & COOH.
\end{array}
$$
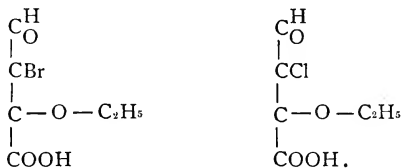
That these ethers are saponified by alkalies while the corresponding phenyl compounds are converted into derivatives of acrylic acid may possibly be due to the great difference in character between the phenyl and ethyl groups.

In other respects the behavior of the two acids finds ready explanation in the hydroxyl formulæ. While we are unable to follow in detail the somewhat complex reaction which ensues when the acids are heated with an excess of baric hydrate, the formation of oxalic, carbonic, and formic acids under these conditions is not unintelligible. The decomposition with aqueous bromine, on the other hand, evidently takes place according to the reaction

$$
\begin{array}{ccccc}
C_O^H & & & C_O^H & \\
| & & & C_{Br_2}^{Cl} & \\
CCl & Br_2 & Br_2 & & \\
-|| \cdots\cdots\cdots\cdots = & & \cdot + 2\,_H^{Br} \\
C-OH & O & H_2 & COOH & \\
| & & & | & \\
COOH & & & COOH &
\end{array}
$$
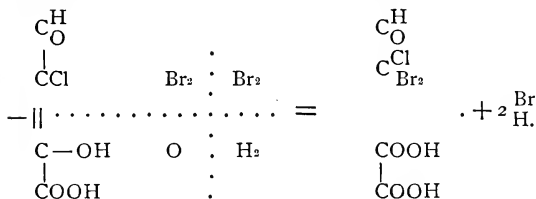
The aniline derivatives are then strictly analogous to the anil-glyoxylic acid of Böttinger,[1]

$$
\begin{array}{lll}
C_{N.C_6H_5}^H & C_{NC_6H_5}^H & C_{N.C_6H_5}^H \\
| & | & | \\
CBr & CCl & COOH. \\
|| & || & \\
C-OH & C-OH & \\
| & | & \\
COOH & COOH &
\end{array}
$$
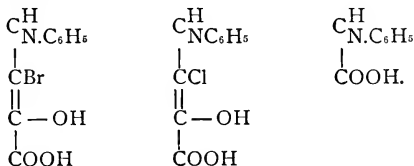
[1] Annalen der Chemie **198**, 222.

That the dibasic character of these compounds has been impaired by the introduction of the aniline residue is but natural, while the persistence of this dibasic character shows that they cannot be derived from the ketone formula by the replacement of the ketone oxygen. A compound of the form

$$C_O^H$$
$$|$$
$$C_H^{Br}$$
$$|$$
$$C = N.C_6H_5$$
$$|$$
$$COOH$$
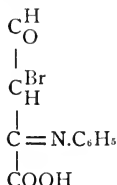
could hardly form dibasic salts.

Moreover, the fact that these aniline derivatives do not form stable condensation products with phenylhydrazine may be taken as further evidence that they contain hydroxyl, and not the ketone or aldehyde group. That we have not yet been able to reverse the reaction, and replace the hydroxyl groups again by the halogens, we cannot but think due simply to the instability of the acids themselves.

While we feel that the constitution of mucoxybromic and mucoxychloric acids is thus determined with reasonable certainty, further investigations upon the subject will be made in this laboratory.

ON THE DETERMINATION OF ARSENIC AS THE PENTASULPHIDE.

By LeRoy W. McCay.

In 1878 Bunsen,[1] in an article upon the separation of antimony from arsenic, showed that by treating an acidified solution of arsenic acid kept alternately hot and cold for a long time, with an excess of sulphuretted hydrogen, and permitting the whole to stand for a day, the arsenic was completely precipitated as the pentasulphide. He recommends this sulphide as an excellent form in which to determine arsenic.

[1] Ann. d. Chem. **192,** 305.

I have of late been experimenting a good deal in connection with the conditions regulating the formation of the highest sulphide of arsenic, and have obtained the same results as those obtained by Bunsen. The precipitate obtained by passing a stream of sulphuretted hydrogen through the acidified solution of an alkali arseniate is undoubtedly pentasulphide of arsenic.[1]

Further, I have discovered a new and rapid method for preparing the sulphide by the action of sulphuretted hydrogen upon arsenic compounds, whereby it is obtained in a state of great purity. Aside from its theoretical importance, the method is of immediate value in its bearing upon the quantitative determination of arsenic. The principal objection to the Bunsen method lies in the long time and large quantities of sulphuretted hydrogen gas necessary to effect a complete separation. Chemists who have had any experience in the matter are well aware of how annoying the sluggish precipitation of arsenic by sulphuretted hydrogen from an arsenic acid solution can be. It will therefore doubtless prove a relief to many to know that a complete precipitation of the arsenic in the form of the pentasulphide is possible in one hour.

Some time ago I published in the *Chemical News*[2] an article upon the reduction of arsenic to arsenious acid by means of strong sulphurous acid, the reduction being accomplished in hermetically sealed bottles and at a temperature corresponding to that of a boiling water-bath. In a subsequent paper, which appeared in this Journal,[3] I showed how the idea could be made the basis of a method for estimating arsenic with great speed and accuracy.

Lately, while engaged in making some determinations of arsenic according to Bunsen's method, the thought struck me that perhaps the long and disagreeable precipitation of the arsenic might be avoided and the separation be easily and rapidly accomplished by making use of the same device employed in reducing arsenic to arsenious acid. A single experiment confirmed my expectations; the precipitation of the element was complete in one hour.[4] Indeed, the bottle had hardly been in the boiling bath a minute before the yellow pentasulphide commenced to come down. The bottle used in all my experiments has a capacity of about 200 cc. The stopper and neck of the bottle were treated with a little fine emery

[1] This is in direct opposition to the statements of Ludwig, Wackenroder, H. Rose, and Fuchs.
[2] **51**, No. 1320, March 13, 1885.　　　[3] **7**, p. 373.
[4] See my preliminary note in the Chem. News **54**, 287.

powder, so as to produce a perfectly air-tight joint. By wetting a small piece of cloth, stretching it down tightly over the stopper and tying the ends firmly to the sides of the neck of the bottle with a piece of cord also wetted, the danger of the stopper being thrown out during the heating is rendered very slight. I have generally thrown a piece of wire gauze over the bath during each experiment, but this is really unnecessary, as I have never yet had a bottle broken by the internal pressure.

A saturated solution of sulphuretted hydrogen, at the ordinary temperature, contains about three times its volume of the gas. 200 cc. of a dilute solution of arsenic acid would then absorb, roughly speaking, $200 \times 3 = 600$ cc. sulphuretted hydrogen gas. But 1000 cc. sulphuretted hydrogen gas $= 1.5199$ grams; consequently 600 cc. gas $= 0.912$ gram. Now, 150 grams As $= 160$ grams $S = 170$ grams H_2S for complete saturation. Hence the quantity of sulphuretted hydrogen absorbed by 600 cc. solution — namely, 0.912 gram — would suffice for precipitating 0.805 gram arsenic. But since the gas must be present in large excess,[1] the amount of arsenic capable of being precipitated as the pentasulphide would be considerably less than 0.805 gram. I have found anything from 0.1–0.3 gram to be a convenient quantity for a determination. The pentasulphide separates out in a thick skin, which adheres but slightly to the bottom and sides of the bottle. If the bottle, when cool, be inclined, the skin loosens itself, and one part can be made to overlap the other in a way which bears a striking resemblance to an omelette. The precipitate can be removed from the bottle without the slightest difficulty. When the sulphide, with the exception of a few particles, has been brought on the filter paper, a little water is put in the bottle, the stopper is inserted and the whole violently shaken for a few moments. Thus the particles are freed from any adhering air, are broken up, and can then be removed from the bottle so completely that not a yellow speck can be detected on the glass. I used for test analyses the following solutions :

1. $\frac{N}{10}$ solution of arsenic acid : This was prepared by oxidising 4.95 grams pure, dry arsenious acid with fuming nitric acid, evaporating, neutralising with ammonia and diluting to a litre.

2. A standard solution of di-hydrogen potassium arseniate : This was prepared by dissolving about 25 grams of the salt in

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[1] See Fresenius, Qualitative Analyse, 15te Auflage.

water and diluting to two litres. By careful analysis 25 cc. =
0.1292 gram As, and 50 cc. = 0.2585 gram As.

The first quantitative experiments were made precisely as follows:

_A._ The solution of arsenic acid was pipetted into the bottle,
diluted to about 150 cc., and rendered strongly acid with concen-
trated hydrochloric acid. The solution was treated with sulphu-
retted hydrogen gas until a decided opalescence made its appear-
ance, when the bottle was closed, the stopper firmly tied down, and
the whole placed in the boiling water-bath and here kept for one
hour. At the end of the hour the bottle was removed from the
bath, allowed to cool, and violently shaken so as to cause the
pentasulphide to subside rapidly, leaving the supernatant liquid
clear. Its contents were then filtered on a weighed filter paper
dried at 110° C. The precipitate was washed with water until a
few drops of the filtrate gave no reaction for chlorine with nitrate
of silver, and then, in regular order, six times with alcohol, four
times with bisulphide of carbon, and again four times with alcohol.
I used the pump in all cases. The drying was done at 110° C.
and to constant weight. Two hours invariably proved sufficient.

Taken.	Calculated.	Found.
I. 20 cc. $\frac{N}{10}$ H₃AsO₄	0.1550 gram As₂S₅	0.1555 gram As₂S₅
	= 0.0750 " As	= 0.0752 " As.
II. 30 cc. $\frac{N}{10}$ H₃AsO₄	0.2325 gram As₂S₅	0.2330 gram As₂S₅
	= 0.1125 " As	= 0.1127 " As.
III. 50 cc. $\frac{N}{10}$ H₃AsO₄	0.3875 gram As₂S₅	0.3871 gram As₂S₅
	= 0.1875 " As	= 0.1873 " As.
IV. 50 cc. $\frac{N}{10}$ H₃AsO₄	0.3875 gram As₂S₅	0.3879 gram As₂S₅
	= 0.1875 " As	= 0.1877 " As.
V. 50 cc. $\frac{N}{10}$ H₃AsO₄	0.3875 gram As₂S₅	0.3875 gram As₂S₅
	= 0.1875 " As	= 0.1875 " As.
VI. 50 cc. $\frac{N}{10}$ H₃AsO₄	0.3875 gram As₂S₅	0.3870 gram As₂S₅
	= 0.1875 " As	= 0.1872 " As.

To see whether the trisulphide, when heated under pressure and
in the presence of excess of sulphuretted hydrogen and a little air,
could be made to take up sulphur and pass partially into the state
of pentasulphide, I made the following experiment: [1]

50 cc. $\frac{N}{10}$ arsenious acid were brought into the bottle, strongly
acidified with hydrochloric acid, and saturated with sulphuretted

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[1] It seemed possible that with the aid of the air remaining in the bottle the pentasulphide
might be formed in accordance with the equation $As_2S_3 + 2H_2S + 2O = As_2S_5 + 2(H_2O)$.

hydrogen. Yellow trisulphide of arsenic was of course immediately precipitated. The bottle was closed and the whole heated in the boiling water-bath for one hour. I obtained, after filtering, washing, etc., 0.3095 gram $As_2S_3 = 0.1887$ gram As, whereas theory demands 0.1875 gram. The result is a trifle high, it is true, but the experiment certainly proves that no pentasulphide can be formed by heating together the trisulphide, sulphuretted hydrogen and *small* quantities of air.

To avoid the use of alcohol and carbon bisulphide in washing the precipitate, I proceeded as follows, and, as will be seen, with complete success:

B. The solution, after having been brought into the bottle and acidified with hydrochloric acid, was diluted with freshly boiled water until the bottle was nearly full, and then saturated with sulphuretted hydrogen. By so doing almost all the air was expelled from the bottle, and a subsequent separation of sulphur from the sulphuretted hydrogen by the action of any free oxygen rendered next to impossible.

The rest of the process was then conducted exactly as has been already described. The sulphide was washed with water until the filtrate was free from chlorine. I found it well, in order to promote the subsequent drying of the precipitate, to replace the water adhering to the same by running a small quantity of alcohol through the filter. This, however, is not necessary.

Taken.	Calculated.	Found.
I. 25 cc. standard $\}$ H_2KAsO_4 $\int$	0.2670 gram As_2S_5 $= 0.1292$ " As	0.2675 gram As_2S_5 $= 0.1294$ " As.
II. 25 cc. standard $\}$ H_2KAsO_4 $\int$	0.2670 gram As_2S_5 $= 0.1292$ " As	0.2671 gram As_2S_5 $= 0.1292$ " As.
III. 25 cc. standard $\}$ H_2KAsO_4 $\int$	0.2670 gram As_2S_5 $= 0.1292$ " As	0.2670 gram As_2S_5 $= 0.1291$ " As.
IV. 50 cc. standard $\}$ H_2KAsO_4 $\int$	0.5340 gram As_2S_5 $= 0.2584$ " As	0.5350 gram As_2S_5 $= 0.2588$ " As.
V. 50 cc. standard $\}$ H_2KAsO_4 $\int$	0.5340 gram As_2S_5 $= 0.2584$ " As	0.5331 gram As_2S_5 $= 0.2580$ " As.
VI. 50 cc. standard $\}$ H_2KAsO_4 $\int$	0.5340 gram As_2S_5 $= 0.2584$ " As	0.5333 gram As_2S_5 $= 0.2581$ " As.
VII. 50 cc. standard $\}$ H_2KAsO_4 $\int$	0.5340 gram As_2S_5 $= 0.2584$ " As	0.5335 gram As_2S_5 $= 0.2582$ " As.
VIII. 50 cc. standard $\}$ H_2KAsO_4 $\int$	0.5340 gram As_2S_5 $= 0.2584$ " As	0.5351 gram As_2S_5 $= 0.2588$ " As.

50 cc. of this standard solution were precipitated under pressure and washed according to the first method, *i. e.* with water, until the filtrate was free from chlorine, then six times with alcohol, four times with bisulphide of carbon, and again three times with alcohol. I obtained 0.5326 gram $As_2S_5 = 0.2578$ gram As. The weight of the sulphide is somewhat below the required figure, but the corresponding amount of arsenic differs from the calculated quantity by only 0.0006 gram. It seemed well to analyse this standard solution by precipitating and weighing the arsenic as the trisulphide.

To do so, I reduced 50 cc. by heating the same with sulphurous acid under pressure, boiled off the sulphurous acid remaining, and precipitated the arsenic with sulphuretted hydrogen. The precipitate was carefully filtered, washed and dried according to Bunsen's directions. I obtained 0.4237 gram $As_2S_3 = 0.2583$ gram As. The amount required is 0.2584 gram As.

To further test this method of determining arsenic, I had a friend make up a solution of arseniate of potassium, such that every 50 cc. contained between 0.1 and 0.3 gram of arsenic. I made two analyses of this solution and obtained (1) 0.1336 gram As, and (2) 0.1331 gram As. The first precipitate was washed as Bunsen directs, the second according to my own method. The calculated result, as I was informed, was 0.1344 gram As. The salt, however, is not absolutely pure, as I have convinced myself by frequent and careful analysis. Allowing for the small amount of impurity, it will be seen that the agreement between the calculated quantity and the results found is entirely satisfactory.

I suggest, then, that when occasion arises for making an estimation of arsenic according to Bunsen's method, the modification here discussed be used. The process is a great improvement upon the Bunsen mode of procedure, for the following reasons: 1. It is remarkably rapid; 2. the quantity of sulphuretted hydrogen necessary for precipitation is reduced to a minimum ; 3. no alcohol nor bisulphide of carbon is necessary for washing; and 4. the pentasulphide does not stick to the sides of the bottle, but separates out in such a state that every trace can be removed without even the aid of a feather.

RESEARCHES ON ALLOISOMERISM.

I.

BY ARTHUR MICHAEL.

There is scarcely a subject in organic chemistry that has attracted more attention and has been more fully investigated than the isomerism of maleic and fumaric, and citra-, ita- and mesaconic acids. The interest shown in the examination of these acids has been largely due to the difficulty that the present theories of structural chemistry find in giving a satisfactory explanation of their constitution. Kekulé,[1] whose brilliant investigation of these acids may be considered as forming the corner-stone of our knowledge of their structure, made an attempt at an explanation, but it can hardly be considered as throwing much light on the subject. It was next considered by H. Kolbe, who in this, as in all other questions relating to isomerism and constitution of organic compounds, showed the keenest insight of any chemist of his time. Kolbe gave maleic and fumaric acids substantially the constitutions at present generally adopted.[2] Somewhat later, Kekulé[3] returned to the subject, and assigned analogous constitutions to the methyl homologues :

$$
\begin{array}{lll}
CH_2-COOH & CH_2-COOH & CH_2-COOH \\
\quad | & \quad | & \quad | \\
C & CH_2 & CH \\
\quad | & \quad \| & \quad | \\
CH_2-COOH. & =C-COOH. & CH-COOH. \\
\text{Itaconic acid.} & \text{Citraconic acid.} & \text{Mesaconic acid.}
\end{array}
$$
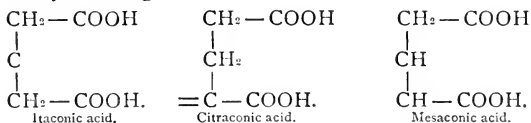
The formulæ of the first two acids were changed by Meilly,[4] in accordance with a better knowledge of the constitution of pyrotartaric acid, to the following :

$$
\begin{array}{ll}
CH_2 & CH_3 \\
\| & \quad | \\
C-COOH & C-COOH \\
\quad | & \quad \| \\
CH_2-COOH. & CH-COOH.
\end{array}
$$

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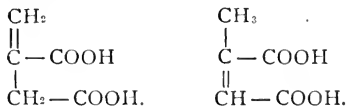
[1] Annalen der Chemie, Suppl. **2**, 114.

[2] Lehrbuch, 1ste Aufl. **2**, 579. Changed in accordance with the present notation, they are represented by CH_2-COOH $\quad CH-COOH$

$\qquad C \quad -COOH \quad$ and $\quad \| $
$\qquad \qquad \qquad \qquad CH-COOH.$

[3] Zeitschrift für Chemie, N. F. **3**, 652.   [4] Annalen der Chemie **171**, 153.

To explain the isomerism of mesaconic acid, Henry[1] and Markownikoff[2] supposed it to be a polymeride of citraconic acid; a view, as Fittig has remarked, that can hardly be upheld, as Hübner and Schreiber[3] had shown that the evidently analogously constituted fumaric and maleic acids have the same molecular weight. Van't Hoff[4] deserves the credit of considering the subject from a new point of view. In his pamphlet on the constitution of organic substances he concluded that the isomerism of maleic and fumaric, and of citraconic and mesaconic, acids cannot be represented by the present views on the molecular constitution of organic compounds, and attempted to show that it may be explained by his ingenious hypothesis concerning the configuration of the molecule in space. This chemist suggested that several other knotty problems of organic chemistry may be explained in the same manner; as the constitution of the two *β*-chlorcrotonic and bromcinnamic acids, as well as those of angelic and tiglinic acids. It is perhaps because van't Hoff made no experimental contribution to the question, and the adopted structural theories permitted what seemed to most chemists a more plausible explanation of these cases of isomerism than that proposed by him, that his views were not adopted. The question was then made by Fittig[5] and his pupils the subject of an elaborate series of investigations. Fittig revived the formulæ of fumaric and maleic acids suggested by Kolbe, and believed that his work confirmed them. He followed a suggestion previously made by Kekulé, which is, that compounds containing a bivalent carbon should form addition products with more readiness than those containing so-called doubly-linked carbons. He showed that Kekulé's previous observation of the greater facility with which maleic and citraconic acids go over into saturated compounds than their isomerides is true in other reactions. These views seem to have been adopted by the majority of chemists, although it was known that a great many organic compounds containing so-called double bonds form addition products with equal facility; indeed, Anschütz[6] has shown that fumaric ether takes up bromine with as great readiness as any maleic compound; and they are evidently based on that curious dogma of double bonds, of the existence of which there is not a

[1] Bull. Soc. Chim. **23**, 347.
[2] Annalen der Chemie **182**, 353.
[3] Zeitschrift für Chemie, N. F. **7**, 712.
[4] La Chimie dans l'Espace.
[5] Annalen der Chemie **188**, 95; **195**, 128, 169; **200**, 87.
[6] Berichte der deutschen chemischen Gesellschaft **13**, 1541.

tittle of satisfactory proof. Finally, as to the latest contributions on the subject I refer to Kekulé and Anschütz's [1] hypothesis that fumaric acid consists of a right and left-handed optically active maleic acid; to Le Bel's [2] geometrical formulæ; to Erlenmeyer's [3] chemical explanation, and to a brief discussion of these and other views on the subject by the writer.[4]

It seemed as if contributions to our knowledge of this intricate case of isomerism might be made in two directions. In the first place, a more exact and general method of distinguishing between acids belonging to the fumaric and maleic acid series was desirable. The present means of distinction, which rests on the capability of the acid of forming an anhydride, means that the operation must be performed at a temperature where intramolecular changes are not unlikely to occur, that a comparatively large amount of the acid must be used, and it is not applicable to a large number of unsaturated acids, the classification of which would doubtless throw light on the constitution of the already classified acids; secondly, an examination of such unsaturated halogen acids as the so-called β-chlor- and β-isochlorcrotonic, and α- and β-brom-cinnamic acids, with a view of bringing indisputable proofs in regard to their constitutions. The present views on the constitution of organic compounds seem to many chemists to represent a state of finality, instead of being only a guide to a better insight; and this is probably the reason why the constitution of so many compounds is accepted without any further proof, simply because their existence is indicated by the present hypotheses. In no part of organic chemistry is this more noticeable than among unsaturated acids and their halogen derivatives, where the constitution of many compounds has been assigned in apparent contradiction to all analogy, simply that their existence may be explained by the present views on chemical isomerism.

A clue to a general method of distinguishing between acids of the fumaric and maleic series was found in an observation made by Gottlieb,[5] that an aqueous solution of the aniline salt of citraconic acid gives citraconanil on boiling, while a solution of the isomeric aniline mesaconate can be evaporated to dryness without undergoing a change. On following this line of investigation, it was

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[1] Berichte **14**, 717; **18**, 1400.
[2] Bull. Soc. chim. **37**, 300.
[3] Berichte der deutschen chemischen Gesellschaft **19**, 1937.
[4] *Ibid.* **19**, 1381; **20**, 554.
[5] Annalen der Chemie **77**, 277.

found that the distinction is general between acids of the fumaric and maleic series, and the results obtained form the subject of the following communications.

I.—A Relation between the Constitution of Polybasic Unsaturated Organic Acids and the Formation of their Anilides.

By Arthur Michael.

Behavior of Maleic Acid towards Aniline.

To a solution of 8 grams of maleic anhydride (1 mol.) in 100 grams of water 7.4 grams of aniline (1 mol.) were added. The aniline went immediately into solution, which was then heated in a water-bath, when presently needles began to separate. After heating for an hour, the contents of the flask were allowed to cool, filtered, and the filtrate heated again, when it gave a further deposit of needles on cooling. The substance was purified by several crystallisations from alcohol, and gave on analysis the following result:

0.2314 gram substance gave 0.6115 gram CO_2 and 0.1145 gram H_2O.

	Theory for $CH - CONHC_6H_5$ $\|$ $CH - CONHC_6H_5$.	Found.
C	72.18	72.07
H	5.26	5.49

The anilide crystallises from alcohol in long white needles that melt at 211°–212°. It is somewhat soluble in hot, sparingly in cold water; readily in hot, pretty soluble in cold alcohol. It is insoluble in dilute mineral acids and alkalies. The formation of the anilide may be represented as follows:

$$CH - COONH_3C_6H_5 \qquad CH - CONHC_6H_5$$
$$\| \qquad\qquad\qquad = \| \qquad\qquad\qquad + 2H_2O.$$
$$CH - COONH_3C_6H_5 \qquad CH - CONHC_6H_5$$
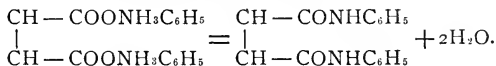
Besides the dianilide of maleic acid, a second substance, which remains in the alcoholic mother liquor, is formed in the reaction. This compound is insoluble in dilute acids and alkalies, and may represent the anil.[1][2]

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[1] I have lately noticed that W. H. Perkin observed the formation of anilides from aqueous aniline maleate about six years ago (Berichte **14**, 2540), and also that aniline fumarate remains unchanged. He made no analyses, and did not follow up the experiments.

[2] This paper, including the note referring to Perkin's observations, was in the hands of the printer when I received a paper by Anschütz and Wirtz (Annalen der Chemie **239**, 137) on the

Behavior of Fumaric Acid towards Aniline.

A dilute aqueous solution containing fumaric acid and aniline, in proportion to form the acid aniline salt, was heated for several days in a flask connected with an upright cooler. No precipitate was formed under these conditions, neither did anything separate from the solution on cooling. It contained unchanged aniline fumarate, and gave a precipitate of fumaric acid on addition of chlorhydric acid. This experiment was repeated with the same result with a concentrated solution of the salt, as well as when aniline in proportion to form the neutral aniline salt was used. If an aqueous solution of acid aniline fumarate is concentrated in an evaporating dish, it will be noticed that towards the end of the operation a precipitate is deposited. This consists of fumaric acid, as both the acid and neutral aniline salts of fumaric acid, when boiled with water, gradually decompose into acid and free base, the latter passing off with the steam.

anilides of fumaric and maleic acids. These chemists have made a detailed investigation of the substance designated as the dianilide of maleic acid, and find that it gives phenylaspartic acid when treated with acids or alkalies. In view of these observations they change the constitution of the anilide to that of the isomeric anil of phenylaspartic acid. The constitution I assigned to the compound was the only one that could be given it at the time of the experiment.

I take this opportunity to explain the mistakes that led Mr. Wing and myself (This Journal **7**, 282) to give the constitution of a fumaric dianilide to the anil of maleic acid. A nitrogen estimation (owing to an erratum .1484 gram of substance was printed instead of .1984 gram) gave 10.19 per cent., a result that agrees fairly well with the amount indicated by theory. A carbon and hydrogen analysis gave 69.24 C and 4.30 H. This analysis was rejected, as everything seemed to point to the impossibility of the substance being an anil. It gave fumaric acid on continued boiling with water, and as there was no ground for supposing the existence of an anil of fumaric acid, the only explanation would have been the conversion of a maleic derivative into fumaric acid by heating with water, which seems very improbable. In the second analysis Mr. Wing made the mistake of adding the increase of weight of the solid caustic potash twice, and thereby got results that agreed with those indicated by the dianilide. Anschütz and Wirtz seem to have overlooked our statement that the compound is decomposed by continued boiling with water into fumaric acid and aniline, and give the existence of the supposed dianilide of maleic acid as a reason for our believing the compound to be an anilide of fumaric acid ; but, as the empirical constitution of the maleic derivative was unknown at the time, it is not likely that this could have entered into our calculations.

Perkin's observation on the formation of the anil of phenylaspartic acid differs from mine, as he heated the dry product to 100°, while I have made a point of showing the anilide formation in the presence of water in my experiments. The fact that an anilide is not formed from aniline mesaconate had already been noticed by Gottlieb, and the formation of citraconanil from a cold solution of aniline citraconate would seem, judging from the observations mentioned in the following paper, to be a mistake. As already stated, Perkin made no analyses, nor did he follow up his observations, and his opinion in regard to the constitution of the maleic acid derivative was based solely on the fact that aniline citraconate under the same conditions gives citraconanil. In view of this it is not a little surprising that Anschütz and Wirtz should endeavor to convey the impression that the views of Perkin and myself on the constitution of the substance conflicted. It would seem as if advantage was taken of circumstances to convey to the reader what seems to me to be almost a misrepresentation of the actual state of affairs.

Behavior of Monobrommaleic Acid towards Aniline.

Monobrommaleic acid (obtained from dibromsuccinic acid by boiling with water, and melting at 128°) was dissolved in about seven parts of water, and an equivalent quantity of aniline added. The base dissolved, and presently a crystalline precipitate separated. This consisted of clusters of plates, melting at $128°–128\frac{1}{2}°$, soluble in dilute chlorhydric acid. They are the acid aniline salt.

0.2592 gram salt gave 0.1665 gram AgBr.

$$\text{Theory for } \underset{|}{C}Br - COONH_3C_6H_5[1]$$
$$CH - COOH.$$

		Found.
Br	27.75	27.30

If this acid salt is dissolved in water, and the solution allowed to stand several days at ordinary temperature, it will be noticed that a crystalline substance gradually separates.

0.2472 gram gave 0.1708 gram AgBr.

$$\text{Theory for } \underset{|}{C}Br - CONHC_6H_5$$
$$CH - COOH.$$

		Found.
Br	29.63	29.36

The compound is the acid anilide of brommaleic acid, and crystallises in prisms. It is insoluble in dilute chlorhydric acid.

The action of aniline on brommaleic acid in the heat gives entirely different results from those obtained by allowing the reaction to proceed in the cold. The solution, on boiling, soon turns yellow, and a crystalline substance begins to separate. This substance is best made by heating a solution of the neutral aniline salt in about thirty parts of water, in a flask connected with an upright condenser, to boiling for about twenty minutes, and filtering the liquid while hot. The yellow precipitate was purified by several crystallisations from alcohol, and was found to be free of bromine.

0.2055 gram substance dried at 100° gave 0.5513 gram CO_2 and 0.0839 gram H_2O.

	Theory for $C_{16}H_{12}N_2O_2$.	Found.
C	72.73	73.10
H	4.55	4.62

The substance crystallises from alcohol as ochre-colored, round clusters of microscopic needles that melt at 229°–230°. It is moderately soluble in hot, sparingly in cold water; in hot alcohol it

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[1] In this, and in a number of other constitutions, it is assumed that the base will unite with the carboxyl of the acid that is most under the influence of negative radicals.

is pretty soluble, less in cold. The substance is insoluble in dilute acids and alkalies, but on standing with dilute solutions of the last reagent it very slowly goes into solution, to form the salt of a different substance, which is precipitated on addition of acids; a result that takes place much more rapidly if warm alkali is used.

The aqueous filtrate from the yellow needles deposits a second substance, mixed with some of the first, on cooling. To separate these substances they may be crystallised from a small amount of water, filtering off the insoluble portion. It is easier, however, to treat the mixture with a very dilute solution of caustic alkali, which dissolves the new substance, leaving the yellow needles behind. The filtrate was carefully neutralised, and the precipitate purified by crystallisation from alcohol. It does not contain bromine.

0.2153 gram substance dried at 100° gave 0.5389 gram CO_2 and 0.102 gram H_2O.

	Theory for $C_{16}H_{14}N_2O_3$.	Found.
C	68.09	68.23
H	4.96	5.27

The substance separates from water as very slightly yellow-colored, round groups of indistinct small crystals that melt at 176°. It is quite soluble in hot, moderately in cold water. Alkalies dissolve it immediately, and the addition of an acid causes a precipitate of the unchanged substance.

These substances stand in a simple relation to phenyl-amido-maleic acid, a substance that may be supposed to be the first product of the action of aniline on brommaleic acid in the heat:

$$CBr — COONH_3C_6H_5 \atop CH — COONH_3C_6H_5 \quad = \quad {CNHC_6H_5 — COOH \atop CH — COOH} \quad + C_6H_5NH_3Br.$$
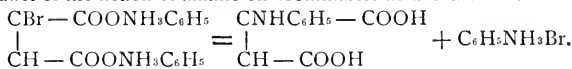
This acid unites with aniline to form a salt, and, being under conditions that make the existence of an aniline salt of a derivative of maleic acid impossible, a condensation takes place:

$$CNHC_6H_5 — COOH \atop CH — COONH_3C_6H_5 \quad = \atop$$

$$CNHC_6H_5 — COOH \atop CH — CONHC_6H_5 \quad (C_{16}H_{14}N_2O_3) + H_2O ;$$

$$CNHC_6H_5 — COOH \atop CH — CONHC_6H_5 \quad = \atop$$

$$CNHC_6H_5 — CO \atop CH \quad — \quad CO {>} NC_6H_5 \quad (C_{16}H_{12}N_2O_2) + H_2O$$
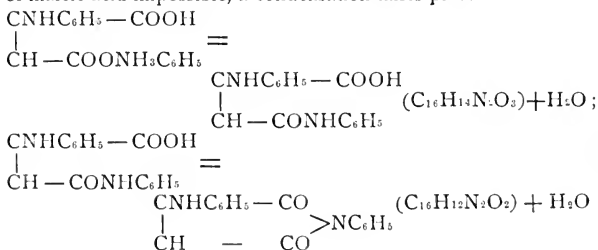
The bright yellow substance, according to this interpretation, is the anil of phenyl-amido-maleic acid, and the pale yellow compound an acid anilide of the same acid.[1]

Behavior of Bromfumaric Acid towards Aniline.

Monobromfumaric acid (melting point $177°$–$178°$: made by heating dibromsuccinic acid and water to $150°$ in a sealed tube, and also by treating brommaleic with fuming bromhydric acid) and aniline in equivalent proportions unite immediately to form the acid aniline salt. This salt is quite insoluble in water, much more so than the corresponding brommaleic acid salt, and by adding aniline to a solution of one part of acid in thirty of water, a copious precipitate soon separates. For analysis it was crystallised from water. It melts at $153°$–$154°$, and is soluble in dilute chlorhydric acid.

0.2697 gram salt gave 0.1750 gram AgBr.

$$\text{Theory for } CBr - COONH_3C_6H_5$$
$$\overset{|}{C}H - COOH.$$

	Theory	Found.
Br	27.75	27.53

[1] Shortly after a preliminary note on this work (Berichte **19**, 1376) was sent to the German Chemical Gazette for publication, I received Part No. 6 of the journal that contained a paper by Reissert and Tiemann (**19**, 626). These chemists had examined the action of aniline on dibromsuccinic acid, and obtained two compounds that are identical with the products obtained from the halogen fumaric and maleic acids. Reissert and Tiemann considered it probable that the anil represented a dipyridylene, but adopted the view presented in my preliminary note after its publication (Reissert, *ibid.* **19**, 1644). I should like to call attention to the constitution of the condensation products of phenyl-amido-pyrotartaric acid, which Tiemann and Reissert have classified as quinoline derivatives. Although they (*Ibid.* **19**, 624) mention that the compounds have the composition of methyl-fumaranilic acid and methyl-fumaranil, they reject the interpretation that their compounds are really the ones named ; but their pyranilpyroinic anhydride has the melting point of citraconanil (98°), and all the properties of that compound. Its formation is very readily understood when we bear in mind that β-amido acids have a tendency to decompose into unsaturated acids and bases, as is shown in the decomposition of β-amido-propionic acid into acrylic acid and ammonia. The formation of citraconanil from phenyl-amido-pyrotartaric acid may be represented by the following equations :

$$CH_3 - C - NHC_6H_5 - CH_2 \quad CH_3 - C - CH$$
$$\overset{|}{C}OOH \qquad \overset{|}{C}OOH = \overset{|}{C}OOH\overset{|}{C}OOH + NH_2C_6H_5 =$$
$$CH_3 - C - CH$$
$$\overset{|}{C}O \quad \overset{|}{C}O + 2H_2O.$$
$$\overset{\vee}{N}C_6H_5$$
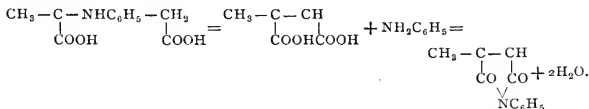
If, as Tiemann and Reissert assert, the so-called pyranilpyroinic acid is formed from citraconanil by alkalies, then this acid is citraconanilic acid ; although the melting point of that acid is 175°, and these chemists give 165° for their product. Perhaps a more detailed investigation will disclose the identity of citraconanilic acid with the acid obtained from their so-called anhydride ; and if the first condensation product should turn out not to be citraconanilic acid, it doubtless has the constitution $CH_3 - C - NC_6H_5 - CH_2$

$$\overset{|}{C}OOH \qquad \qquad \overset{|}{C}O$$
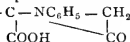
This salt shows a much greater stability than the corresponding brommaleic derivative. It may be allowed to stand with water for weeks without undergoing a change, and its solution in water does not give, on long standing, a precipitate of an anilide. If a solution of the salt is boiled for about ten minutes, a yellow precipitate begins to form, which becomes quite copious on long boiling. The solution, after boiling about an hour, was filtered hot, and the yellow precipitate crystallised several times from alcohol. The substance melted at 229°-230°, and agreed in its properties with the yellow substance obtained by heating a solution of aniline brommaleate. In order to explain its formation it is necessary to assume that phenyl-amido-fumaric acid at the temperature of boiling water changes into the alloisomeric phenyl-amido-maleic acid, which in the presence of aniline decomposes into the anil.

Behavior of Chlorfumaric Acid towards Aniline.

Five grams of monochlorfumaric acid (melting point 183°: obtained by the action of phosphorus pentachloride on tartaric acid) were dissolved in one hundred grams of water, and two and one-half grams of aniline added. The aniline went into solution, and presently a crystalline substance separated. For analysis it was crystallised twice from alcohol.

0.2736 gram air-dried substance gave 0.1610 gram AgCl.

$$\text{Theory for } \underset{\underset{\text{CH}-\text{COOH}}{|}}{\text{CCl}-\text{COONH}_3\text{C}_6\text{H}_5}$$

		Found.
Cl	14.57	14.55

Acid aniline chlorfumarate crystallises from alcohol as white monoclinic prisms with domes, that melt at 178°, but begin to turn yellow at about 170°. It is difficultly soluble in cold water and alcohol, but readily in chlorhydric acid, when it decomposes into chlorfumaric acid and aniline chlorhydrate. This salt or its aqueous solution may be allowed to stand for weeks with water without undergoing any change. An aqueous solution of the salt behaves on boiling like the corresponding bromfumaric acid salt ; only its conversion into the anil of phenyl-amido-maleic acid proceeds with less readiness. When a solution of the salt is boiled a number of minutes, the unchanged salt is deposited on cooling. If the boiling is continued for some time the solution gradually turns yellow, and the yellow anil begins to separate. This was purified as

already described, and gave the same compound as obtained from brommaleic and bromfumaric acids.

0.1573 gram substance gave 0.4195 gram CO_2 and 0.0677 gram H_2O.

$$\text{Theory for } CNHC_6H_5-CO \atop CH \qquad -CO > NC_6H_5.$$

		Found.
C	72.73	72.76
H	4.55	4.79

The formation of the same compound from brommaleic, brom- and chlorfumaric acids when aqueous solutions of their neutral aniline salts are boiled is of considerable theoretical importance, as it implies the conversion of derivatives of fumaric acid into a maleic acid compound at the temperature of boiling water, a fact that can only be brought in harmony with Fittig's views of the constitution of these compounds with the assumption of improbable inter-molecular changes. I shall return to the subject in a discussion of the bearings of the present investigation on the constitution of the acids in question.

Behavior of Dibrommaleic Acid towards Aniline.

This reaction is complicated and, according to the conditions of the experiment, a number of different products are formed, which, however, are difficult to obtain in a pure state.

To a solution of the acid in thirty parts of water an equivalent proportion of aniline was added. The base dissolved, and imme-diately the very difficultly soluble acid aniline dibrommaleate was deposited. This salt dissolves in dilute chlorhydric acid, to form the free acid and aniline chlorhydrate. If it is allowed to stand under water for a number of days it gradually loses water to form an anilide, which decomposes when heated with water or other sol-vents, and could not be obtained in a state suitable for analysis. The neutral salt, formed on adding two equivalents of aniline to a solution of one of the acid, is also quite insoluble. It dissolves in dilute chlorhydric acid. When allowed to stand under water for a long time it also passes over into an anilide that may be separated from any unchanged salt by treating with dilute chlorhydric acid. This salt when heated in a solvent goes over into a mixture of a yellow substance that is described further on, and unchanged sub-stance. As it was found impossible to crystallise the substance

without its undergoing a partial change, it was dried in a vacuum and analysed.

0.2224 gram substance gave 0.2041 gram AgBr.

<div style="text-align:center">

Theory for $\overset{|}{\underset{}{\text{CBr}}} - \text{CONHC}_6\text{H}_5$
</div>

$$\text{CBr} - \text{CONHC}_6\text{H}_5.$$

	Br		Found.
	37.73		38.98

The substance probably contained a small amount of the anil, but the analysis is sufficiently close to show that the product analysed consisted largely of the dianilide. It was obtained as plates that melted at 138°–140°. The anil is probably obtained by crystallising the anilide, obtained from the acid aniline salt, from ligroin. The solution, on cooling, deposited large white plates, but as they were mixed with yellow needles, and as no satisfactory way could be found to separate the two compounds, no analyses were made. It melts at 160°–162°, and is insoluble in dilute chlorhydric acid.

The yellow compound may be obtained in a pure state by heating three parts of acid in sixty parts of water and 2.2 parts of base for about half an hour, and filtering hot from the reddish yellow precipitate. This was extracted with a small amount of hot alcohol that dissolves some of the substance and most of the dark impurities. The residue was purified by three crystallisations from hot alcohol.

0.1949 gram substance dried at 100° gave 0.1066 gram AgBr.
0.2285 gram substance dried at 100° gave 0.1260 gram AgBr.

<div style="text-align:center">

Theory for $\text{CNHC}_6\text{H}_5 - \text{CO}$ $\Big\rangle \text{NC}_6\text{H}_5$.
$\overset{|}{\text{CBr}} \quad - \text{CO}$
</div>

	Br	Found.
	23.29	23.32 23.46

The anil crystallises from alcohol as flat prisms with end-faces generally at right angles, but in some crystals they obliquely truncated the sides. They melt (under decomposition) at 182°–183°. When large the crystals have a reddish yellow color, but as a powder or as very small crystals it is almost pure yellow. They are insoluble in hot water, and only moderately soluble in hot alcohol. Dilute chlorhydric acid and dilute alkalies do not dissolve them.

$$\begin{array}{l} \text{CBr} - \text{COONH}_3\text{C}_6\text{H}_5 \\ | \\ \text{CBr} - \text{COONH}_3\text{C}_6\text{H}_5 \end{array} + \text{NH}_2\text{C}_6\text{H}_5 =$$

$$\begin{array}{l} \text{CNHC}_6\text{H}_5 - \text{CO} \\ | \qquad\qquad \Big\rangle \text{NC}_6\text{H}_5 + 2\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{NH}_3\text{Br}. \\ \text{CBr} \qquad - \text{CO} \end{array}$$
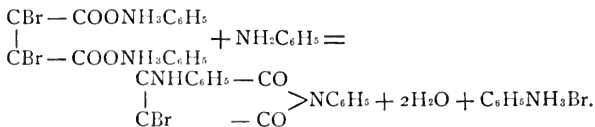
The formation of this substance is of interest because it shows that dibrommaleic acid can hardly have the commonly accepted constitution. If both the bromine atoms were united with the same carbon there is every reason for supposing that a substance free of halogen would have resulted from the reaction, as the compound

$$CBr - NHC_6H_5 - CO$$
$$\underset{C}{|} \qquad \qquad -CO \qquad >NC_6H_5 \text{ would, judging from what}$$

we know of the properties of this class of substances, hardly show the stability of the substance in question, but would decompose into a substance free of halogen and bromhydric acid.

A substance free of halogen and crystallising as dark red plates may be obtained by heating the acid in aqueous solution with a large excess of aniline. I did not succeed, however, in getting it into a state suitable for analysis.

Behavior of Bromcitraconic Acid towards Aniline.

Bromcitraconic anhydride (melting point 99°–100°) was dissolved in twenty parts of water, and an equivalent of aniline added to the solution. The base dissolved and a crystalline precipitate was immediately deposited. This substance was filtered, washed with water, and analysed.

0.2461 gram substance dried in vacuum gave 0.1556 gram AgBr.

$$\text{Theory for } CH_3 - C - COOH$$
$$\underset{CBr - COONH_2C_6H_5.}{|}$$

	Theory	Found.
Br	26.91	26.50

The acid aniline bromcitraconate crystallises in clusters of small white rhombic plates that melt at 120°–121°, turning yellow. It is soluble in dilute chlorhydric acid, but careful neutralisation of the solution with ammonia throws down the original substance. It is somewhat soluble in cold water.

If this salt is allowed to stand under water for a few hours, or its solution in water heated for a minute, it passes over into the anil.[1] The substance was purified by crystallisation from alcohol.

0.2630 gram substance dried at 100° gave 0.1871 gram AgBr.
0.3071 "   "   "   "   "   " 0.2197 "   "

$$\text{Theory for } CH_3 - C - CO$$
$$\underset{CBr - CO}{|} >NC_6H_5.$$

	Theory	Found.
Br	30.07	30.26 30.41

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[1] Through a mistake on my part this substance was represented as the acid anilide in the preliminary note, Berichte **19**, 1373.

It crystallises in stellar groups of prismatic needles that melt at $144.5°–145.5°$, and are insoluble in cold, slightly in warm water. They are readily soluble in hot, moderately in cold alcohol, and are insoluble in dilute chlorhydric acid.

$$CH_3 — C — COOH \atop \underset{CBr — COONH_3C_6H_5}{|} \quad = \quad CH_3 — C — CO \atop \underset{CBr — CO}{|} \Big> NC_6H_5 + 2H_2O.$$
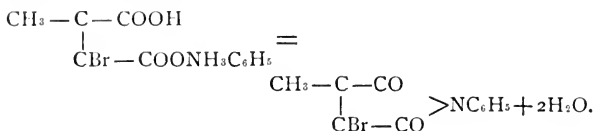
Behavior of Aconitic Acid towards Aniline.

The importance of the aniline reaction for ascertaining whether an unsaturated polybasic organic acid belongs to the maleic or fumaric acid series is shown when the classification of acids like aconitic, which decompose into simpler products on heating, is in question. That the method based on the formation of anhydrides cannot be used in such cases is obvious ; but, as the following experiments indicate, the behavior of an aqueous solution of the aniline salts of such acids is adapted to show to which series they belong.

An aqueous solution of dianiline aconitate, when boiled in a flask connected with a condenser, soon deposits an oily substance, mixed with some yellow needles. After the formation of the precipitate ceased to increase, it was separated from the mother liquor and extracted with a little hot alcohol, which dissolved the amorphous substance. The residue was crystallised three times from alcohol.

0.1237 gram substance gave 0.323 gram CO_2 and 0.0545 gram H_2O.

	Theory for $C_{15}H_{14}N_2O_3$.	Found.
C	70.59	71.13
H	4.57	4.91

The substance crystallises in very light yellow fine needles that melt at $250°–252°$.[1] It is insoluble in water, sparingly soluble in hot alcohol. The very small yield of this substance obtained did not permit further examination. It may be identical with the anilide obtained by Pebal[2] by heating aniline aconitate to $140°$, as its properties agree with those of the compound obtained by that chemist. The amorphous mass that is the principal product of the

[1] In the preliminary note the melting point of a less pure product was given at $215°–217°$.
[2] Annalen der Chemie **98**, 81.

reaction could not be brought into a crystalline form.   It is insoluble in dilute chlorhydric acid, and is possibly an anilide of the acid.

Far better results were obtained by allowing an aqueous solution of the dianiline salt to remain for some time at ordinary temperature.   An amorphous substance also separates in this instance, but in equal quantities a crystalline substance.   To separate them the precipitate was extracted with cold alcohol, when most of the amorphous substance went into solution.   The residue was then crystallised four times from alcohol.

0.2102 gram substance, dried at 100° C. in vacuum, gave 0.5134 gram CO_2 and 0.1028 gram H_2O.

0.3334 gram substance, dried at 100° C. in vacuum, gave 23 cc. N at 765.2 mm. and 19° C.

	Theory for $C_{18}H_{16}O_4N_2$.	Found.
C	66.69	66.60
H	4.94	5.43
N	8.64	8.15

The substance crystallises in long prismatic needles that have a very faint pinkish cast and melt at 188°–189°.   They are insoluble in hot water and dilute chlorhydric acid, but dissolve in alkalies ; in hot alcohol they are pretty soluble, moderately in the cold solvent.   Strong chlorhydric acid dissolves the substance in the cold, but the addition of water to the solution gives a precipitate of the original substance.   The substance is formed from the dianiline salt by elimination of two molecules of water.[1]

It is evident from these results that aconitic acid belongs to the maleic and not to the fumaric acid series.[2]   I shall return to the importance of this conclusion in regard to the constitution of maleic acid in another paper.

Behavior of Citra- and Itaconic Acids towards Secondary and Tertiary Aromatic Amines.

According to an observation made by Gottlieb,[3] an aqueous

[1] It would be premature to assign structural formulæ to these compounds, although it is very likely they stand in the relation of anilides to the acid. The formation of substances that are insoluble in dilute chlorhydric acid from aqueous solutions of the aniline salt is evidently sufficient to classify the acid as belonging to the maleic series. It is my intention, however, to have these compounds made the subject of a detailed examination.

[2] I have lately made some aconitic acid by heating the ether with strong chlorhydric acid in a sealed tube at 100°, when the pure acid separates on cooling. This product is quite insoluble in pure ether, while the acid obtained by heating citric acid is generally represented to be very soluble in that solvent. Is it possible that the first product represents the aconitic acid of the fumaric series ? The subject deserves further investigation.

[3] Annalen der Chemie **77,** 292.

solution of monoethyl-aniline citraconate can be evaporated to dryness, and the residue heated to melting, without undergoing a change. It will be shown in the following paper that all primary aromatic amines having basic properties give anilides when aqueous solutions of their citraconic acid salts are heated, and it seemed of interest to examine secondary and tertiary aromatic amines in their behavior towards the new reagent, as a convenient method of separation could probably be based on the results.

A solution of the acid, as well as the neutral, monoethyl-aniline citraconate can be gently warmed without any change, but on boiling the solution it will be noticed that the base is readily given off; in fact, a dilute aqueous solution of these salts when boiled to dryness is free of base, and the residue contains nothing but citraconic acid. The formation of an anilide when the base was not allowed to escape was never noticed, although the boiling was continued for a long time and very concentrated solutions were used. It was noticed, however, that solutions of the salts which were clear in the cold gave, on warming, a deposit of methyl-aniline ; a proof that the decomposition of the salts into base and acid takes place at the temperature of boiling water. Similar experiments were then made with monoethyl-aniline salts, and exactly the same results were obtained. A dilute aqueous solution of the salt when boiled down to dryness is free of base, and a solution made in the cold sets the base free when heated to 100°.[1]

The dimethyl- and diethyl-aniline salts of citraconic acid are probably represented by the solutions obtained by saturating a strong aqueous solution of citraconic acid with the bases in the cold, but these compounds are so unstable that dilution suffices to decompose them into base and acid, and by heating the mixtures the base volatilises readily with the steam.

The ethyl derivatives of paratoluidine behaved exactly like the corresponding aniline compounds towards citraconic acid.

To a solution of 2.4 grams of citraconic acid in 10 grams of water, 3.4 grams of diphenylamine were added, and the mixture was then boiled for an hour. On cooling the diphenylamine separated unchanged, and was completely soluble in dilute chlorhydric acid.

[1] I am unable to explain the results obtained by Gottlieb with this salt, but suspect that he did not use pure ethylaniline, which, at the time of his experiments, was extremely diffi- cult to obtain in a pure state.

As itaconic acid forms only an acid anilide with aniline, it was thought possible that this acid might give an anilide with mono-methyl and ethyl-aniline, but experiments showed that it acts exactly like citraconic acid toward these bases.

On these results a method of detecting and separating primary aromatic amines from secondary and tertiary amines was based. It is only necessary to dissolve the basic mixture in a solution of citraconic acid, then add an equal volume of citraconic acid to the solution, and boil in a flask with a reversed cooler for several hours. The flask is then connected with a condenser and the contents rapidly distilled almost to dryness, when, if oil-drops still go over towards the end of the operation, more water is added, and the operation repeated. The residue in the flask contains all the primary amines as anilides, and the bases may be obtained as chlorhydrates by decomposing the precipitate with strong chlor-hydric acid. If the mixture contains secondary and tertiary amines which are not volatile with steam, the precipitate is treated with dilute chlorhydric acid, when they dissolve, leaving the anilide unchanged. It is not unlikely that the method may be used for a quantitative separation. For detecting a primary aromatic amine a small amount is treated as above in a test-tube, the solution boiled several minutes, replacing the water if necessary, and cooled. If a precipitate is formed that does not completely dis-solve in dilute chlorhydric acid, the presence of a primary base may be considered as proved.[1]

Behavior of Acetic and Succinic Acids towards Secondary and Tertiary Aromatic Bases.

The results obtained with citraconic acid were the reason for an examination of the behavior of acetic and succinic acids, as types of fatty mono- and dibasic acids, towards aromatic bases.

Glacial acetic acid and aniline, in equivalent proportions, form, at ordinary temperature, a clear solution of aniline acetate. If this

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[1] It is evident that other unsaturated acids, as itaconic or phthalic acids, may be used. I have experimented with citraconic acid as it seemed best adapted for the purpose, and can be made in large quantities without trouble. It is also apparent that the reaction may be used for detecting acids belonging to the maleic acid series, and in some instances to separate them from other organic acids. With acids like citra-, itaconic, and phthalic, the separation is almost quantitative. There is no doubt that the reaction will prove of considerable use, not only in the investigation of basic aromatic mixtures, but also in studying the decomposition products of organic polybasic acids.

solution is kept under 30° it remains perfectly clear, but above that temperature it begins to become turbid, owing to the separation of minute oil-drops. It increases in turbidity up to 50°, above which temperature it gradually becomes less turbid, and finally perfectly clear at about 60°. On cooling the solution these phenomena are reversed. This remarkable behavior is evidently due to the presence of a small amount of a base in so-called pure aniline, that has weaker basic properties than aniline itself. This view is corroborated by the following observation. If some water is added to aniline acetate the separation of a small amount of oil takes place, although the solution shows a strong acid reaction. The oil dissolves again when about three times as much water is added as the volume used of aniline acetate.[1]

An aqueous solution of aniline acetate, when boiled gradually, decomposes, and at first free aniline passes off; after this, a distillate that remains clear on cooling, which, as it contains both base and acid, evidently is aqueous aniline acetate ; and, finally, acetic acid. I have tried a number of aniline salts of volatile fatty acids, and believe that the relation just described may be considered as a general one.

Mono- and dimethyl-aniline, and also the ethyl derivatives, dissolve in the equivalent amount of glacial acetic acid ; but it is a matter of doubt whether it is more than simple solution, as the addition of water causes the base to separate. On the differences in their behavior towards acetic acid a separation of primary amines from the secondary and tertiary bases was based. The basic mixture is dissolved in an excess of glacial acetic acid, three times the volume of water added, the mixture heated, and the oil separated from the solution of primary acetate. It is doubtful, however, whether this method is as exact as the one previously described.[2]

Succinic acid (6 grams) was dissolved in a small quantity of lukewarm water, and methylaniline (5 grams) added. On cooling, most of the base separated from the solution, which was filtered. The solution is clear at ordinary temperature, but becomes turbid, owing to the separation of an oil at about 30°. When boiled, methylaniline escapes, leaving a solution of pure acid.

[1] It is doubtful whether perfectly pure aniline has ever been made. The oil may be amidothiophene, and its investigation is certainly of interest. I shall attempt to obtain it in sufficient amount to ascertain its nature.

[2] This method can of course only be used to separate those primary aromatic amines that form salts with acetic acid.

Behavior of Citraconic Acid towards Fatty Amines.

That the formation of anilides from primary aromatic bases and citraconic acid stands in a close relation to the comparatively weak basic properties of the substances is shown by the behavior of mono-, di- and triethyl-amine citraconates. The acid and neutral salts of these bases may be evaporated to dryness without undergoing any decomposition. A solution of amidoacetic acid in citraconic acid may be boiled without forming an anilide. On evaporating to dryness a residue soluble in water was obtained, but it is uncertain whether it was a citraconate or simply a mixture of the two substances. Aspartic acid does not combine with organic acids.[1]

II.—A Relation between the Constitution of Polybasic Unsaturated Organic Acids and the Formation of their Anilides.

By A. Michael and G. M. Palmer.

Behavior of Maleic Acid towards Aniline.

It was shown in the preceding paper that an aqueous solution of aniline maleate, on boiling, gives maleic dianilide. A different result is obtained when a solution of acid aniline maleate in ten parts of water is allowed to stand in the cold. After standing a day a crystalline substance was deposited from the solution, which was filtered and the operation repeated until no further deposit is formed. The crystals were purified by repeated crystallisation from alcohol, and are the acid anilide of maleic acid.

0.1746 gram substance gave 0.4025 gram CO_2 and 0.0875 gram H_2O.

Theory for $CH - CONHC_6H_5$
$$\overset{|}{C}H - COOH.$$

		Found.
C	62.82	62.91
H	4.71	5.56

The anilide crystallises from dilute alcoholic solutions in almost white prismatic plates, from concentrated solution in plates whose

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[1] The best method of making aspartic acid from asparagine is to boil that substance with alkalies until ammonia ceases to come off, and then acidulate with acetic acid, when all the aspartic acid is precipitated.

end-faces are imperfectly developed. The crystals melt at 207°. It is soluble in hot water and alcohol, moderately in cold alcohol. Dilute chlorhydric acid does not dissolve it, but it is soluble in dilute aqueous alkalies.   Its formation is represented thus :

$$\begin{array}{l} \text{CH} - \text{COONH}_3\text{C}_6\text{H}_5 \\ | \\ \text{CH} - \text{COOH} \end{array} = \begin{array}{l} \text{CH} - \text{CONHC}_6\text{H}_5 \\ | \\ \text{CH} - \text{COOH} \end{array} + 2\text{H}_2\text{O}.'$$
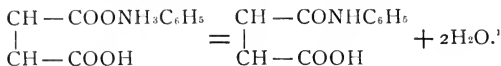
Behavior of Citraconic Acid towards Aniline.

An aqueous solution of mono-aniline citraconate behaves like the maleic acid compound, when it is allowed to stand in the cold.   The solution deposits more or less rapidly, according to its dilution, large white crystals, which were crystallised from alcohol.

0.3175 gram substance gave 0.7531 gram CO_2 and 0.1532 gram H_2O.

Theory for $\text{CH}_3 - \text{C} - \text{CO} - \text{NHC}_6\text{H}_5$

	$\overset{|}{\text{CH}} - \text{COOH.}$	Found.
C	64.39	64.67
H	5.36	5.37

The compound forms large white rhombic prisms which melt at 175°. It is insoluble in cold water and dilute chlorhydric acid, but dissolves in dilute alkalies to form salts, and acids precipitate the unchanged substance from such solutions.   It is soluble in hot alcohol, moderately in cold.

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[1] In view of the differences in the results obtained by Anschütz and Wirtz (Annalen **239,** 148), I repeated this experiment, unfortunately on a small scale, as I had but a few grams of maleic acid at my disposal. The compound separates as crystalline plates that are soluble in dilute chlorhydric acid, but after several crystallisations from alcohol become insoluble in it, in fact they are insoluble in the strong acid. It is evident that the compound undergoes some change during crystallisation, and I am surprised that Anschütz and Wirtz did not take the trouble to crystallise their product before making note of supposed differences, as it is evident that reference was made in our preliminary note to the crystallised product. In regard to the melting point, the specimen I examined decomposed partially before that temperature is reached, so that it is impossible to give a well-defined melting point. The substance dissolves in dilute alkalies, but strong alkaline solutions set aniline free. An analysis of the product gave the following figures :

0.2878 gram substance dried in a vacuum gave 0.6087 gram CO_2 and 0.150 gram H_2O.

	Theory for $C_{10}H_{11}NO_4$.	Found.
C	57.41	57.68
H	5.26	5.76

The product analysed by Mr. Palmer was probably dried in vacuo at 100°, when it lost a molecule of water, although, as no mention is made in his notes of the conditions of drying, this must remain a surmise on my part. Whether the compound is the acid anilide with a molecule of water of crystallisation, can only be settled by a more detailed examination.—A. M.

The substance, obtained by Gottlieb[1] by treating citraconanil with ammonia and precipitating the solution with acetic acid, may be identical with our compound, but, as there are two isomeric acid anilides of citraconic acid possible, the identity must be left to be decided by a more detailed account of Gottlieb's compound, who mentions that a small yield was obtained by his method, while by the method just described almost the theoretical yield can be obtained. Gottlieb describes his compound as small, glittering crystals. A solution of dianiline citraconate does not form an anilide on standing in the cold, but on boiling the anil separates. It melts at 98°.

Behavior of Itaconic Acid towards Aniline.

Anschütz and Petri[2] and also Markownikoff[3] have observed that itaconic acid or its silver salt, when treated with acetyl chloride, gives an anhydride of the acid. This reaction cannot be considered as a proof that itaconic acid belongs to the maleic acid series, as the method used also causes the formation of anhydrides with acids that certainly do not belong to it, as succinic and pyrotartaric acids. The following experiments on the behavior of itaconic acid towards aniline show quite conclusively, however, that it is to be classified as a member of the maleic series.

Five grams of itaconic acid were dissolved in 50 grams of water, and 3 grams of aniline added. This solution was heated to boiling for half an hour, in a flask connected with a condenser, and on cooling gave a copious precipitate, which was purified by crystallisation from dilute alcohol.

0.3664 gram substance gave 0.8657 gram CO_2 and 0.1804 gram H_2O.

	Theory for $CH_2 - C - CO - NHC_6H_5$ $\quad\quad\quad \lvert$ $\quad\quad\quad CH_2 - COOH.$	Found.
C	64.39	64.45
H	5.36	5.44

It crystallises in plates that melt at 189°, and is identical with the product obtained by Gottlieb[4] by heating solid acid aniline itaconate. It is insoluble in dilute chlorhydric acid, but dissolves in dilute alkalies, and is precipitated unchanged from this solution by adding an acid.

[1] Annalen der Chemie **77**, 280.   [2] Berichte der deutschen chemischen Gesellschaft **13**, 1538.
[3] *Ibid.* **13**, 1844.   [4] Annalen der Chemie **77**, 284.

The same compound is formed by allowing a solution of acid aniline itaconate in ten parts of water to stand for several days in the cold, when rhombic prisms that melt at 189° are deposited. It was impossible to obtain the anil of itaconic acid by heating an aqueous solution of its aniline salts.

Behavior of Citraconic Acid towards some other Aromatic Primary Amines.

It seemed to be of interest to ascertain whether other primary aromatic amines than aniline would show similar reactions with citraconic acid, and to what degree the basic property of the amine could be decreased without its losing the power of giving the anilide reaction.

A solution of acid paratoluidine citraconate in five parts of water gives, on warming, a crystalline precipitate that melts at 161°, and when crystallised from absolute alcohol melted at 166°. This compound is probably the acid toluide. When it is crystallised several times from boiling water it is converted into a different substance, which is the tolil.

0.3670 gram substance gave 0.9625 gram CO_2 and 0.1885 gram H_2O.

0.3631 gram substance gave 0.9552 gram CO_2 and 0.1815 gram H_2O.

$$\text{Theory for } CH_3 - \underset{CH - CO}{\overset{C - CO}{\Big|}} > NC_6H_4 - CH_3.$$

		Found.	
C	71.64	71.50	71.71
H	5.46	5.69	5.56

Citracontolil crystallises from water in long silky needles that melt at 114.5°. It is insoluble in dilute chlorhydric acid and alkalies, soluble in alcohol and hot water, sparingly soluble in cold water.

Mono-ortho-toluidine citraconate dissolves readily in cold water. This solution becomes turbid on boiling, and if the heating is continued for about half an hour an oil separates. On cooling, a further quantity of oil was deposited, that on standing gradually became solid. It was insoluble in dilute chlorhydric acid, and was evidently a toluidide.

α-Naphthylamine citraconate in aqueous solution gives an oily precipitate on boiling, which solidifies on standing. The compound

crystallises from alcohol as yellow plates that melt at 141° and
may be sublimed unchanged. The compound is insoluble in
dilute chlorhydric acid and alkalies, and probably represents citra-
con-naphthylimide.

A solution of β-naphthylamine citraconate also deposits a sub-
stance on boiling. This compound, crystallised from water, forms
yellow feathery needles that melt at 170° and may be sublimed
without change. It is insoluble in dilute chlorhydric acid.

The behavior of metamido-benzoic acid towards citraconic acid
is of particular interest, as this substance is so weak a base that it
does not form salts with monobasic organic acids. A solution of
one part of citraconic acid in five of water dissolves metamido-
benzoic acid (equivalent proportions) very slowly in the cold,
rapidly on warming. When this solution is boiled a crystalline
precipitate is soon deposited, which was purified by crystallisation
from hot water.

0.3802 gram substance gave 0.8710 gram CO_2 and 0.1366 gram
H_2O.

$$\text{Theory for } CH_3-C-CO \atop CH-CO {>} N-C_6H_4.COOH.$$

	Theory	Found.
C	62.33	62.46
H	3.89	4.00

Meta-citraconanil-carboxylic acid crystallises from water as fine
prismatic needles that melt at 218°. It is soluble in hot alcohol
and water, sparingly soluble in cold water, and insoluble in dilute
chlorhydric acid. Dilute solutions of alkalies dissolve it to form
salts.

Although it did not seem likely that citraconic acid would form
an anilide with sulphanilic acid, as this amido compound does not
even form salts with mineral acids, an experiment was made that
gave negative results. Corresponding to the anilides, derivatives
of phenylhydrazine have been obtained by using analogous
methods. Our expectation that phenylhydrazine would form an
azide on heating with aqueous citraconic acid was fulfilled. A
solution of monophenylhydrazine citraconate in ten parts of water,
when boiled, turns yellow, and a crystalline precipitate soon sepa-
rates, which is considerably increased as the solution cools. It was
purified by crystallisation from alcohol.

0.3903 gram substance gave 0.9441 gram CO_2 and 0.1851 gram
H_2O.

$$\text{Theory for } CH_3 - C - CO \atop \underset{CH - CO}{\big|} > N_2HC_6H_5.$$

		Found.
C	65.34	65.89
H	4.95	5.24

It crystallises in long, bright yellow prismatic needles that melt at 160°, and are sparingly soluble in cold, pretty soluble in hot water, and readily in hot alcohol. It is insoluble in dilute chlorhydric acid. As citraconic acid does not form anilides with secondary amines, the reaction is very likely correctly expressed by the following equation :

$$CH_3 - C - COON_2H_4C_6H_5 \atop \underset{CH - COOH}{\big|} =$$

$$CH_3 - C - CO \atop \underset{CH - CO}{\big|} > N - NH - C_6H_5 + 2H_2O.$$
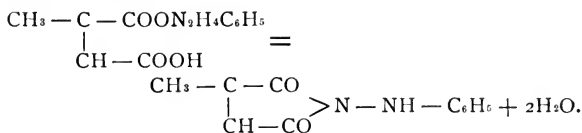
Behavior of the Phthalic Acids towards Aniline.

The phthalic acids are distinguished by the capability of the ortho acid of forming an anhydride. All attempts to obtain a similar derivative of the other two acids have been futile. As the ease that polybasic acids form anhydrides evidently is in close relationship with the anilide reaction, and ortho-phthalic acid forms its anhydride with readiness, it seemed of interest to examine whether this reaction would not serve to distinguish between these isomeric acids.

The acid aniline phthalate is difficultly soluble in cold, but dissolves readily in hot water. If a solution of this salt in six parts of water is boiled in a flask connected with a cooler, it will be noticed that a precipitate gradually separates from the hot solution, that increases as the solution cools. The acid aniline salt is readily decomposed by dilute chlorhydric acid, forming the chlorhydrate and free acid, while the precipitate formed by boiling a solution of the salt is insoluble in that acid. It melts at 203°, and agrees in all its properties with phthalanil. The anil is also formed by boiling an aqueous solution of the neutral aniline salt, and when a solution of the acid salt is allowed to stand at ordinary temperature for some days.

Isophthalic acid also forms an acid aniline salt, but its solution in water may be boiled for hours without anything separating

from it, and on cooling yields unchanged salt that is readily soluble in dilute chlorhydric acid. An aqueous solution of the neutral aniline salt gave the same result.

Terephthalic acid unites with aniline, but with difficulty, and the salt is unstable in presence of considerable water. A solution in a small quantity of hot water was boiled for an hour without any change taking place, and a like result was obtained by heating an aqueous solution of the neutral salt.[1]

Behavior of some Saturated Polybasic Acids towards Aniline.

It seemed desirable to show that the property of forming anilides on heating an aqueous solution of aniline salts is characteristic of a certain group of unsaturated acids, and not shown by polybasic saturated fatty acids. We shall make but a brief mention of our experiments in this direction, and include in it several experiments with unsaturated acids. Acid aniline oxalate is difficultly soluble in hot water. After boiling its aqueous solution for a long time, long flat prisms separate on cooling. They are soluble in dilute chlorhydric acid, and consist of unchanged salt.

Acid aniline malonate dissolves readily in cold water. Its solution undergoes no change on boiling.

Acid aniline succinate is difficultly soluble in cold water, but dissolves in hot. It undergoes no change when its aqueous solution is boiled.

One part of tartaric acid in ten parts of water will dissolve sufficient aniline to form the acid salt. On boiling this solution a precipitate separates. This, however, represents an aniline tartrate, as it is immediately decomposed by dilute chlorhydric acid.

Acid aniline citrate is soluble in cold water, and does not change when its aqueous solution is boiled.

Acid aniline camphorate dissolves in boiling water, and after cooling separates unchanged as an oil that gradually solidifies.

Acid aniline pyrotartrate (obtained by reducing citraconic acid) is soluble in hot water, and undergoes no change when its aqueous solution is boiled.

Acid and neutral aniline mucates do not form anilides when their aqueous solutions are boiled.

[1] There is no doubt but that a very convenient method for detecting the presence of carboxyls in ortho position in aromatic acids can be based on their forming anilides from aqueous solutions of their aniline salts. The existence of a second orthophthalic acid that would stand in the same relation to orthophthalic acid that fumaric does to maleic acid also seems probable.

Summary.

I. Unsaturated polybasic organic acids may be divided into two classes according as their aniline salts, in aqueous solution, split off water to form anilides or remain unchanged. The anilide-forming acids are classified as belonging to the maleic acid series, and the others to the fumaric acid series.

II. Of the acids as yet examined the following belong to the maleic series: maleic, brommaleic (m. pt. 128°), dibrommaleic acid (123°), citraconic, itaconic, bromcitraconic, aconitic and ortho-phthalic acids. To the fumaric series: fumaric, bromfumaric (178°), chlorfumaric (191°), mesaconic, mucic, camphoric, and iso- and terephthalic acids.

III. Chlor- and bromfumaric acids, in aqueous solution, when boiled with aniline are converted into the anil of phenyl-amido-maleic acid.

IV. The bromine atoms of dibrommaleic acid are symmetrically grouped.

V. The acids of the maleic series give the anilide reaction with all primary salt-forming aromatic amines, but not with secondary or tertiary aromatic bases. On this property a method of separating these bases has been based.

VI. The acetates of primary amido-benzenes are not decomposed by cold water, while those of the secondary or tertiary amines, if formed at all, are decomposed. A separation of basic mixtures has been based on these properties.

VII. Saturated polybasic acids do not give the anilide reaction.[1]

VIII. The results obtained in this investigation cannot be brought in harmony with the hypothesis that acids of the maleic series contain a divalent carbon.

IX. The anhydride and anilide formation of orthophthalic and similar acids probably depends on their belonging to the maleic series, and not on the positions of the carboxyls as represented by the constitutional formulas now in use.

X. Aqueous solutions of the citraconates of fatty amines do not form alkylamides.

Tufts College, Mass.

[1] This rule is certainly not without exceptions, as experiments with the aniline salts of the dibenzyldicarboxylic acids have shown, which will be published later. The behavior of aniline salts of polybasic organic acids in their aqueous solution will be continued, and I wish to reserve the further examination of the reaction until my research is completed.

ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON THE ETHERS OF ORGANIC ACIDS, AND ON SOME DERIVATIVES OF ACETIC ACID.

By Arthur Michael.

Organic chemistry is indebted to A. Cahours[1] for the introduction of one of its most valuable reagents. The French chemist showed that phosphorus pentachloride acts on aromatic acids, forming the corresponding chlorides, and on aromatic aldehydes to form compounds in which the oxygen of the carbonyl is replaced by two chlorine. The great importance of the discovery was shown a few years later by Gerhardt,[2] in whose hands the chlorides were made the starting-point of those famous researches on organic anhydrides and amides. Gerhardt also obtained, by a modification of Cahours' reaction, the chlorides of fatty acids; and Würtz[3] and Geuther[4] showed that phosphorus pentachloride acts on ethyl aldehyde to form ethylidene chloride. Friedel[5] proved that the oxygen of acetone can be replaced by two chlorine by means of the reagent, and Schischkoff and Rösing[6] that benzoyl chloride can be converted into phenyl-chloroform by heating it with the pentachloride in a sealed tube, a reaction that Hübner[7] found to be also applicable to acetyl chloride. These reactions have been shown to be typical for the groups of organic substances they represent by other chemists, and it is now generally considered that, with a few exceptions of complicated products, substances containing hydroxyl may be converted by the chlorides of phosphorus into derivatives in which the hydroxyl is replaced by chlorine, and those containing carbonyl into derivatives in which the carbonyl oxygen is replaced by two chlorine.

There is, however, a noticeable exception to the latter rule in the behavior of organic ethers towards phosphorus pentachloride. Cahours in his paper remarks that phosphorus pentachloride does not react on benzoic ether. On the other hand, Geuther[8] obtained two chlorcrotonic acids by treating the product of the action of

[1] Ann. Ch. Phys. [3] **23**, 327.

[2] *Ibid.* [3] **37**, 285 ; Gerhardt and Chiozza, Comptes rend. **37**, 86.

[3] Ann. Ch. Phys. [3] **59**, 104.   [4] Annalen der Chemie **105**, 321.

[5] Bull. Soc. Chim. 1859, 26.   [6] Compt. rend. **46**, 367.

[7] Annalen de Chemie **120**, 330.   [8] Zeitsch. für Chemie, 1871, 237.

phosphorus pentachloride on acetylacetic ether with water, a result
that indicates the formation of the chlorides of these acids; and
Richter[1] obtained the chloride of monoethyl-oxalic acid by heating
oxalic ether with the same reagent. In view of the stability of
alkyloxyl in ethers, as was shown by Cahours, who obtained the
chloride of anisic acid by the action of phosphorus pentachloride
on the acid, and by Henry[2] on the fatty series, it seemed not un-
likely that the alkyloxyl of the ethers of organic acids would show
a certain, although relatively less, stability than these groups do in
the ethers ; and, bearing this in mind, the product obtained by
Richter may be supposed to represent a secondary stage of the
reaction, it being formed by the decomposition of a substance
formed from oxalic ether by replacing an oxygen by two chlorine :

$$\begin{array}{ll} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + PCl_5 = \begin{array}{ll} CCl_2OC_2H_5 \\ | \\ COOC_2H_5 \end{array} + POCl_3 \ ;$$

$$\begin{array}{ll} CCl_2OC_2H_5 \\ | \\ COOC_2H_5 \end{array} = \begin{array}{ll} COCl \\ | \\ COOC_2H_5 \end{array} + C_2H_5Cl.$$
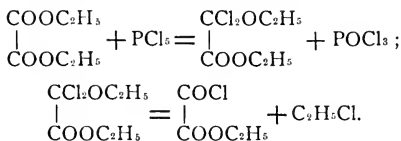
It seemed of interest to ascertain whether this is the true con-
ception of the reaction, and also to ascertain whether other ethers
would not yield such intermediate products, when examined
in view of their instability. If the reactions proceed in this
manner, it is evident that the aromatic ethers of acids would show
a greater stability than the corresponding alkyl derivatives ; as, to
take an example, it is obvious that the phenyl of the compound
$R — CCl_2OC_6H_5$ would be much less likely to separate from the
oxygen than the ethyl of $R — CCl_2 — OC_2H_5$. My experiments
began with phenyl acetate, as it seemed likely that the reaction
would be less complicated with the ether of a monobasic acid than
with the ether of a dibasic acid.[3]

[1] Berichte der deutschen chemischen Gesellschaft **10,** 2228.

[2] *Ibid.* **2,** 276, 664, 710 ; **3,** 704.

[3] A preliminary note on this work was sent to the Berichte for publication on the 17th of
March, 1886, and was published on the 10th of May. On the 28th of May Anschütz and
Schönfeld sent in a short paper to the same journal (page 1444) in which they showed that
one of the carbonyl oxygen of amyl and propyl oxalates may be replaced by means of phos-
phorus pentachloride by chlorine. Although I was pleased to have my views on the action
the pentachloride on organic ethers confirmed, I must express my surprise that these chemists
did not deem it an obligation towards me to send in their results, which they distinctly state
were completed when my note appeared, immediately after the appearance of my note, instead
of waiting longer than two weeks before doing it.

Action of Phosphorus Pentachloride on Phenyl Acetate.

Phosphorus pentachloride does not act on phenyl acetate in the cold, but readily at a moderate heat. A mixture of the substances, in molecular proportions, was brought into a flask connected with a cooler and heated at 100° for four hours. The evolution of chlorhydric acid began soon after heating, and was practically ended after heating two hours, although a very small quantity of the gas continued to be given off on longer heating. In one experiment the evolution of acid continued fifteen hours, but a larger yield of the product of the reaction is not obtained by continuing the operation. The homogeneous liquid was then distilled until a good part of the phosphorus oxychloride and trichloride that are formed in the reaction was driven off, and the residue poured into a considerable amount of cold water. After the violent reaction accompanying the conversion of the chlorides into acids was over, the heavy oily residue was separated from the supernatant liquid, and boiled for several hours, in a flask connected with an upright cooler, with a strong solution of caustic soda. This operation decomposed unchanged phenyl acetate and phenyl phosphate, which is also formed in the reaction. The alkaline mixture was then treated with steam as long as an oil passed over. If, however, cold water was used in the condenser, the substance often came over as a solid. The oil solidified on cooling to a mass of large white crystals, and the solid substance was purified by crystallising four times from a small amount of hot alcohol. The analyses gave the following results:

0.2635 gram substance dried in vacuum gave 0.4170 gram CO_2 and 0.0583 gram H_2O.

0.2712 gram substance dried in vacuum gave 0.5210 gram AgCl.

	Theory for $C_8OCl_3H_5$.	Found.
C	42.95	43 16
H	2.23	2.52
Cl	47.65	47.53

The substance crystallises from alcohol in large stellate groups of crystals, but if a relatively large proportion of alcohol is used, long white needles are deposited. It melts at 26.5° without decomposition. It is insoluble in cold and hot water, readily in hot, pretty soluble in cold alcohol, and also dissolves easily in hot

chloroform, ligroin and benzene, but less in these solvents when cold. The substance passes over readily with steam, and, as its preparation indicates, it can be boiled with strong alkali without undergoing a change. It distills at a high temperature with partial decomposition, but unchanged in a vacuum, the boiling point being 120° under a pressure of 26 mm., and 106°–108° under a pressure of 12 mm. The formation of a substance having the composition $C_8OCl_3H_5$ from phenyl acetate and phosphorus penta-chloride necessitates the assumption that the carbonyl oxygen is replaced by chlorine in the operation; but the hydrogen of the compound thus formed (it is also possible that the two reactions are simultaneous) is extremely susceptible to chlorination, although an excess of unchanged phenyl acetate is evidently present. To form a correct idea of the changes that take place in this remarkable reaction, the various stages that may be supposed to occur are represented by equations:

$$CH_3 - COOC_6H_5 + PCl_5 = CH_3 - CCl_2OC_6H_5 + POCl_3 ;$$
$$CH_3 - CCl_2OC_6H_5 + 2PCl_5 =$$
$$CHCl_2 - CCl_2OC_6H_5 + 2PCl_3 + 2HCl ;$$
$$CHCl_2 - CCl_2OC_6H_5 = CCl_2 - CClOC_6H_5 + HCl.$$
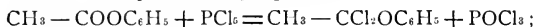
The compound is therefore trichlor-phenoxyethylene or trichlor-vinyl-phenyl ether, and is analogous in its chemical nature to the substance obtained by Geuther[1] by the action of sodium ethyl oxide on perchlorethylene:

$$CCl_2 - CCl_2 + NaOC_2H_5 = CCl_2 - CClOC_2H_5 + NaCl.$$
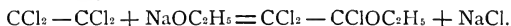
If this view of the constitution of the new substance be correct, it can be synthesised in an analogous manner; that is, by the action of perchlorethylene on sodium phenyl oxide. To realise this synthesis it is not necessary to prepare sodium phenyl oxide, as a solution of phenol in alcoholic sodium ethyl oxide acts as the first-named reagent, and in all probability contains it—in fact, that it gives the result described below may be accepted as a decisive proof:

$$C_2H_5ONa + C_6H_5OH = C_2H_5OH + NaOC_6H_5.$$

An absolute alcoholic solution of sodium, phenol and perchlor-ethylene, in equivalent proportions, was heated for eight hours in a sealed tube at 110°–115°.[2] The product of the reaction was

[1] Jr. prkt. Chem. [2] **7**, 105.

[2] If sodium ethyl oxide and phenol are used in larger proportion and the tube heated to a higher temperature, different products seemed to be formed, which were not further examined.

thrown into water, the mixture extracted with ether, and the ethereal solution, after drying over calcium chloride, heated on a water-bath until the ether was expelled. The residue was distilled under a pressure of 10–12 mm., and passed over almost completely from 105°–107°, which is the boiling point of trichlor-phenoxyethylene. An analysis showed it to be that substance.

0.2186 gram oil gave 0.4731 gram AgCl.

	Theory for $CCl_2CClOC_6H_5$.	Found.
Cl	47.65	47.31.

The formation of trichlor-phenoxyethylene from perchlor-ethylene conclusively proves the accepted constitution as correct, and the reaction may be represented as follows:

$$CCl_2 — CCl_2 + NaOC_6H_5 = CCl_2 — CClOC_6H_5 + NaCl.$$
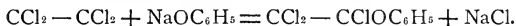
It was assumed that the formation of trichlor-phenoxyethylene was preceded by that of a substance of the constitution $CCl_2H — CCl_2OC_6H_5$. Such a compound would, when treated with alkalies, decompose into chlorhydric acid and the final product of the reaction. It seemed of interest to ascertain whether the elimination of chlorhydric acid takes place in the reaction or during the treatment with alkalies, and with this object in view, a portion of the product of the action of phosphorus pentachloride on phenyl acetate was directly distilled in a vacuum. The portion passing over between 120°–130° under 25 mm. pressure was fractionated again under the same conditions, and passed over principally between 121°–125°, a temperature that corresponds to the boiling point of trichlor-phenoxyethylene. A portion of this oil,[1] which agreed in its properties with the trichlor compound, was analysed.

0.2439 gram oil gave 0.4546 gram AgCl.

	Theory.	Found.
Cl	47.53	46.12

The product obtained by direct distillation probably contained a small amount of a substance with a less percentage of chlorine, and having very nearly the same boiling point as trichlor-phenoxyethylene, but there can be no doubt that the substance analysed was largely composed of the compound. The formation

[1] Pure trichlor-phenoxyethylene, after a distillation in a vacuum, remains an oil at ordinary temperature. It would seem as if a slight decomposition takes place that lowers its melting point.

of the substance in this manner shows that it is a direct product of the action of phosphorus pentachloride on phenyl acetate.[1]

Action of Phosphorus Pentachloride on Metaphenylene Acetate.

It seemed of interest to ascertain whether the acetyl derivatives of polyatomic phenols would behave towards the pentachloride in a manner similar to the phenol derivative.

A mixture of metaphenylene acetate and pentachloride, in the proportion of one molecule of the first to two molecules of the second compound, was heated in a water-bath as long as chlorhydric acid was given off. The product of the reaction was thrown into water, the residue heated with strong alkali, and finally treated with steam. An oily substance passed over that soon solidified. This was crystallised four times from alcohol, and analysed with the following results:

0.2770 gram substance dried in a vacuum gave 0.6453 gram AgCl.

0.2128 gram substance dried in a vacuum gave 0.4495 gram AgCl.

	Theory for $C_6H_4 < ^{OCCl-CCl_2}_{OCCl-CCl_2}$.	I.	Found.	II.
Cl	57.72		57.61	57.53

The formation of the substance, meta-trichlorvinyl-phenylene ether, may be represented as follows:

$$C_6H_4 < ^{OOC-CH_3}_{OOC-CH_3} + 6PCl_5 =$$
$$C_6H_4 < ^{OCCl-CCl_2}_{OCCl-CCl_2} + 2POCl_3 + 4PCl_3 + 6HCl.$$
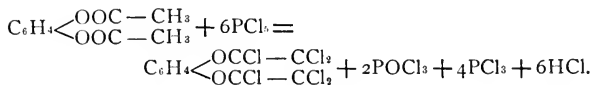
It crystallises from alcohol in long prisms with domes that melt at $53°$–$54°$. It is insoluble in hot water, readily soluble in hot, pretty soluble in cold alcohol. From a warm alcoholic solution it separates on cooling as an oil that often remains liquid until touched with a solid substance. The substance is quite soluble in cold benzene, ligroin, chloroform, and ether.

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[1] It might be supposed that a larger proportion of pentachloride to phenyl acetate would greatly increase the yield of trichlor-phenoxyethylene. Experiments using two and three molecules of chloride to one of acetate showed, however, that the amount thus obtained was not very much greater than when but one molecule of chloride is used. In fact, considering the ease with which phenyl acetate may be made, it would seem more advantageous to use molecule for molecule than to use the chloride in larger proportion.

Action of Phosphorus Pentachloride on Paraphenylene Acetate.

The reagents, two molecules of chloride to one of acetate, were treated as in the corresponding experiment with the meta-acetate. Instead, however, of heating with alkali, the crude product of the reaction was directly treated with steam, when long white needles passed over. These were purified by several crystallisations from alcohol, and analysed.

0.2447 gram substance dried in a vacuum gave 0.3570 gram CO_2 and 0.0550 gram H_2O.

0.2464 gram substance gave 0.450 gram AgCl.

	Theory for $C_6Cl_3H_5O_2$.	Found.
C	40.01	39.78
H	2.09	2.48
Cl	44.47	45.12

The substance crystallises in long white fibrous needles that very closely resemble asbestos in form and appearance. It is slightly soluble in hot water, from which it separates as needles on cooling. In ether, chloroform, and benzene it dissolves readily in the cold, in hot alcohol very soluble, it is also quite soluble in cold. From a saturated hot alcoholic solution it separates in plates. It also dissolves readily in hot ligroin, but only moderately in the cold solvent. Warmed with caustic alkalies it goes into solution and does not separate from the solution on cooling, but the addition of an acid causes a precipitate of the original substance. In acetyl chloride it dissolves with the evolution of chlorhydric acid and formation of an acetyl derivative. It melts without decomposition at 66°–66.5°, but decomposed completely in an attempt at distillation.

The properties of this substance show that it contains a free hydroxyl; in fact, but one of the acetyl groups of the mother substance has undergone the change characteristic for the reaction, and the second unchanged group has been removed by the action of water, probably on treating the crude product with steam.

$$C_6H_4{<}{{OOC-CH_3}\atop{OOC-CH_3}} + 3PCl_5 =$$
$$C_6H_4{<}{{OCCl-CCl_2}\atop{OOC-CH_3}} + POCl_3 + 2PCl_3 + 3HCl;$$

15

$$C_6H_4 \underset{\displaystyle OOC-CH_3}{\overset{\displaystyle OCCl-CH_3}{<}} + H_2O =$$

$$C_6H_4 \underset{\displaystyle OH}{\overset{\displaystyle OCCl-CCl_2}{<}} + CH_3COOH.$$
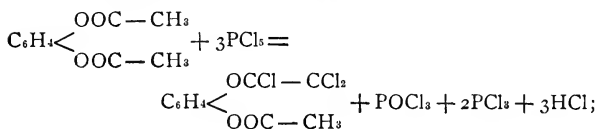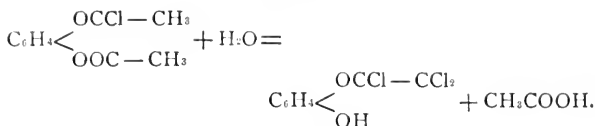
It may be called paroxy-trichlor-phenoxyethylene.[1]

Action of Phosphorus Pentachloride on Phenyl Propionate.

In order to show that the reaction is general for aromatic ethers of other acids, a few preliminary experiments were made on the action of phosphorus pentachloride on phenyl propionate.

Twenty grams of the ether and fifty-eight grams of penta-chloride were heated in a water-bath for twelve hours, the product thrown into water, and the oily residue heated with dilute alkali. On treating with steam, an oil passed over that could not be brought into a solid state. It was fractionated under 25 mm. pressure, when most of it passed over between 110° and 135°. By repeated fractionation it was separated into two portions, one boiling 115°–117° under 25 mm. pressure, and the other from 125°–130°. The chlorine estimations of the oil boiling at 115° gave results that agree with the constitution $C_9H_8OCl_2$.

0.2971 gram substance gave 0.3837 gram AgCl.
0.2613   "   "   "   0.3402   "   AgCl.

	Theory for $C_9H_8OCl_2$.	Found.
Cl	32.41	31.95 32.15

The oil resembles trichlor-phenoxyethylene in its properties, but would not solidify even at 0°.   It is insoluble in water, but readily soluble in alcohol.   Its constitution is probably $CH_3 - CCl - CClOC_6H_5$:

$$CH_3 - CH_2 - COOC_6H_5 + 2PCl_5 =$$

$$CH_3 - CCl - CClOC_6H_5 + POCl_3 + PCl_3 + 2HCl.$$
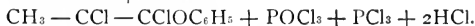
The fraction boiling between 125°–130° was very likely not a pure substance.

0.2543 gram oil gave 0.3967 gram AgCl.

	Theory for $CH_2Cl-CCl-CClOC_6H_5$.	Found.
Cl	42.01	38.57

[1] In a preliminary notice on this reaction (Berichte **19**, 846), I gave this compound the isomeric constitution $C_6H_4 \overset{O}{\underset{O}{>}} CCl - CHCl_2$. At the time of its publication I was unaware that the substance dissolves unchanged in alkalies and also forms an acetyl derivative—properties that exclude such a constitution.

Action of Phosphorus Pentachloride on Ethyl Benzoate.

Cahours in his memoir describes an experiment consisting of distilling the pentachloride with benzoic ether, which he found to pass over unchanged. This result was probably obtained by rapid distillation, when a part of the ether may escape without being acted on. The ether dissolves the chloride when heated to 100°, but even at that temperature a reaction takes place, although very slowly, as after two days' heating most of the chloride separated out of the solution on cooling. If the solution is heated to 110° the reaction also proceeds slowly, so that several days are necessary before a few grams of the pentachloride are completely converted into the oxychloride. At 140° in a sealed tube a much shorter time is needed ; heating for about eight hours in a sealed tube sufficed to convert ten grams of pentachloride into oxychloride. The same products of the reaction were obtained in both cases. When the experiment was made in a sealed tube, the tube opened under pressure, and an inflammable gas was given off that contained chlorine and evidently consisted of ethyl chloride. The greater part of this compound remained in solution, and was given off when the liquid was heated to 40° or 50°. The contents of the tube were subjected to fractionation in a vacuum (12 mm.) and were easily separated into two fractions. The lower-boiling portion consisted of phosphorus oxychloride and the higher of benzoyl chloride, of which almost the amount indicated by theory was obtained. The action of the pentachloride on benzoic ether may be represented as follows :

$$C_6H_5COOC_2H_5 + PCl_5 = C_6H_5COCl + C_2H_5Cl + POCl_3.$$

Action of Phosphorus Pentachloride on Acetic Ether.

The ether and chloride, the first compound in excess, were heated in a sealed tube to 150°. On opening the tube ethyl chloride escaped, and by repeated fractionation of the liquid, unchanged ether, acetyl chloride, and phosphorus oxychloride were obtained.

An experiment with ethyl trichlor-acetate and pentachloride, heated in an oil-bath to 150°, showed that in this instance an analogous reaction took place. Trichlor-acetyl chloride, phosphorus oxychloride, and ethyl chloride were formed.

Remarks on the Preceding Experiments.

The results just described, although in no instance was a com-
pound formed from an organic ether by replacing the carbonyl
oxygen by chlorine, prove the point in question with the same
degree of precision as if such a product had been isolated.   The
formation of trichlor-phenoxyethylene, and analogous substances,
can be explained only by supposing that the carbonyl oxygen of
the aromatic ethers was replaced by chlorine, forming deriva-
tives of the general constitution $R — CCl_2OR$; but owing to the
remarkable facility with which the pentachloride acts on this com-
pound as an agent for chlorination, these derivatives could not be
isolated.[1]   These results leave but little doubt that the penta-
chloride also acts on alkyl ethers to form similar derivatives, but
the point of decomposition of these products seems to be so near
that of chemical action that it is likely that only in a few
instances it will be found possible to isolate the intermediate pro-
ducts.

Not alone is this indicated by the results described in this paper,
but our knowledge of the ease with which the carbonyl oxygen
of the different members of the COOR group enters into reactions
points to the same conclusion.   From this point of view it is neces-
sary to consider the formation of the chloride as the second phase
of the action of phosphorus pentachloride on an organic ether :

$$R — COOR + PCl_5 = R — CCl_2OR + POCl_3 ;$$
$$R — CCl_2OR = R — COCl + RCl.$$
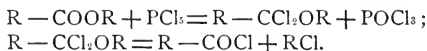
It may be of interest to call attention to the fact that the formation
of an acid chloride from an acid and pentachloride is also open to
the same interpretation ; at least it has become imperative that
more conclusive experiments be made before the present view can
be considered as proved :

$$R — COOH + PCl_5 = R — CCl_2OH + POCl_3 ;$$
$$R — CCl_2OH = R — COCl + HCl.$$
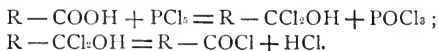
The formation of chlorides by the action of dehydrating agents

[1] I have made some experiments with phenyl benzoate and phenyl acetate, at a lower tem-
perature than that described in the experiments described, that indicate the formation of this
class of compounds, but owing to work of greater importance I have not found time to con-
tinue them.   I hope to continue the investigation at some future time.

and chlorhydric acid on organic acids may be considered to consist of an addition and subsequent dehydration:[1]

$$R - COOH + HCl = R - C \underset{\diagdown OH}{\overset{\diagup OH}{-}} Cl \ ;$$

$$R - C \underset{\diagdown OH}{\overset{\diagup OH}{-}} Cl \ + P_2O_5 = R - COCl + 2HPO_3.$$
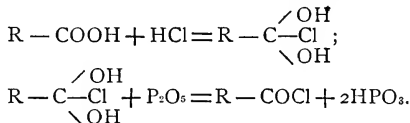
Action of Phosphorus Pentachloride on Acetyl Chloride.

The ease with which phosphorus pentachloride replaces the hydrogen of the methyl in phenyl acetate suggested similar experiments with derivatives of acetic acid. Hübner[2] had already examined the action of the pentachloride on acetyl chloride, but in a sealed tube and at a high temperature. He obtained trichloracetyl chloride, ethenyl chloride, and pentachlor-ethane as products of the reaction.

Forty grams of acetyl chloride and two hundred grams of phosphorus pentachloride were heated in a flask connected with an inverted cooler for several weeks. The action proceeded slowly, and a considerable amount of pentachloride remained unchanged. The product was thrown into water, extracted with ether, and the extract, after drying, subjected to a fractional distillation. By repeating the operation a number of times, it was found possible to separate a portion boiling at 185°–187° that turned solid on cooling and melted at 62°–63°, and consisted of monochloracetic acid. A second fraction boiled between 193°–195°, and on cooling gave crystals melting at 52°. This compound was trichlor-acetic acid. Between these fractions a liquid was obtained that, although it could not be obtained pure, undoubtedly consisted largely of dichlor-acetic acid.

Action of Phosphorus Pentachloride on Monochloracetic Acid.

This reaction takes place much more readily than in the preceding instance. Ten grams acid and eighty-eight grams pentachloride (one molecule acid to four molecules chloride) were

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[1] L. Henry (Berichte **10**, 2043) suggested a somewhat similar explanation for the formation of organic ethers by the action of chlorhydric acid on a mixture of acid and alcohol.

[2] Annalen der Chemie **120**, 330 ; also Samosasky, Zeits. Chem. 1870, 105 ; and Frederici, Berichte der deutschen chemischen Gesellschaft **11**, 1971.

heated in a flask, and after twenty hours the chloride was entirely decomposed. The product was thrown into water, when a neutral oil remained, which was shaken out with a solution of sodium carbonate, dried, and fractionated a number of times. In this way an oil boiling from 120°–122° was isolated, which agrees in its properties with perchlorethylene.

0.1836 gram oil gave 0.6339 gram AgCl.

	Theory for C_2Cl_4.	Found.
Cl	85.24	85.39

Besides perchlorethylene, higher-boiling products are formed, probably consisting of tetra- and pentachlorethene. On extracting the aqueous solution, obtained by pouring the product of the reaction into water, with ether, and fractionating, trichloracetic acid was separated :

$$CClH_2 — COOH + 3PCl_5 =$$
$$CCl_2 — CCl_2 + 2POCl_3 + PCl_3 + 3HCl.$$
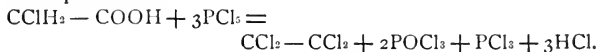
Action of Phosphorus Pentachloride on Phenoxyacetic Acid.

Fifteen grams of acid and sixty grams of pentachloride were mixed in a flask connected with a cooler. A reaction takes place immediately, which is probably due to the formation of the chloride of the acid. The flask was then heated in a water-bath as long as chlorhydric acid came off, an operation that took about fifteen hours. On cooling, about one quarter of the amount of chloride taken separated. The product was thrown into water and filtered from the solid and oily substances that separated. This was treated with steam, when the oil passed over, and was found to consist of trichlor-phenoxyethylene. The residue remaining in the flask was crystallised four times from hot water.

0.2214 gram substance gave 0.1761 gram AgCl.
0.2485 "   "   "   0.1954   "   "

	Theory for $CH_2OC_6H_4Cl — COOH$.	Found.	
Cl	19.04	19.60	19.46

The substance consists of rhombic prisms with domes that melt at 151°–152° without decomposition. It is moderately soluble in hot, sparingly in cold water. In alkalies it is soluble, and is precipitated out of the solution by addition of an acid. The substance has either the constitution $CH_2OC_6H_4ClCOOH$ or $CHClOC_6H_5COOH$, but the first constitution is probably correct, as its alkaline solution

may be boiled without eliminating chlorine. It is therefore monochlor-phenoxyacetic acid :

$$C_6H_5O - CH_2 - COOH + 3PCl_5 =$$
$$C_6H_5O - CCl - CCl_2 + 2POCl_3 + PCl_5 + 3HCl ;$$
$$C_6H_5O - CH_2 - COOH + 2PCl_5 =$$
$$C_6H_4ClOCH_2 - COCl + POCl_3 + PCl_3 + 2HCl.$$
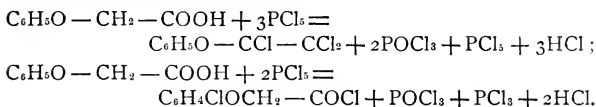
Tufts College, Mass.

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ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON ACETANILIDE.

By Arthur Michael.

The investigations of Gerhardt[1] and Wallach[2] on the action of phosphorus pentachloride on anilides and alkyl amides have shown that the oxygen of the carbonyl is replaced by chlorine, but that these compounds are not very stable, and decompose into compounds having the general constitution $R - CClNR$ and chlorhydric acid. Wallach, to whom we are principally indebted for the investigation of these interesting reactions, found that even the secondary products of the reaction are not stable in the heat, but pass over into basic substances free of chlorine. The investigation of the action of phosphorus pentachloride on the aromatic ethers of acetic acid led me to believe that an analogous reaction might be realised by the action of the pentachloride on anilides, and I made a few experiments with acetanilide in that direction, which, although they have not resulted in the synthesis of the anticipated class of substances, are not without interest. Forty-eight grams of pentachloride (3 mols.) were brought into a flask connected with a condenser, cooled with ice, and ten grams of powdered acetanilide (1 mol.) added. After the reaction, that takes place in the cold, when, as Wallach has shown, the compound $CH_3 - CClNC_6H_5$ is formed, the flask was allowed to stand at the ordinary temperature as long as chlorhydric acid came off, and the reaction was then completed by heating on a water-bath. The homogeneous mass— all the pentachloride was used up—was poured into water, when an oily mass remained undissolved that soon solidified. This

[1] Ann. Ch. et Phys. [3] **53**, 302.   [2] Annalen der Chemie **184**, 1 ; **214**, 193, 257.

substance was purified by crystallising from alcohol, and gave the
following figures on analysis:

0.2458 gram substance gave 0.4258 gram CO_2 and 0.0804 gram
H_2O.

0.2490 gram substance gave 0.3525 gram AgCl.

0.2734 gram substance gave 0.3827 gram AgCl.

	Theory for $C_8H_8Cl_2N_2$.	Found.	
C	47.29	47.24	
H	3.94	4.21	
Cl	34.97	··· 34.94	34.64

The substance crystallises from alcohol in large white mono-
clinic prisms that melt undecomposed at 116.5°–117°. It sublimes
slowly at 100°, forming small prisms with truncated end-faces. In
water, cold and hot, it is insoluble, very soluble in warm, fairly in
cold alcohol.

The substance has neutral properties, it being insoluble in acids
as well as alkalies.

The action of pentachloride on acetanilide gives an entirely
different result if, instead of heating on a water-bath, the mixture
is allowed to remain in a moderately warm place for a long time.
The mixture of pentachloride and anilide, in the same propor-
tions as in the preceding experiment, was first cooled off on ice,
and then allowed to stand at a temperature of about 35° for a
week, when the greater part of the pentachloride was decomposed.
It was noticed that after a number of days a yellow crystalline
substance began to separate from the clear supernatant liquid.
The contents of the flask were poured into water, and the insoluble
residue purified by four crystallisations from alcohol.

I. 0.2621 gram substance gave 0.5522 gram CO_2 and 0.107 gram
H_2O.

II. 0.2482 gram substance gave 0.5251 gram CO_2 and 0.1029
gram H_2O.

III. 0.2534 gram substance gave 0.3172 gram AgCl.

IV. 0.2015 gram substance gave 0.2529 gram AgCl.

	Theory for $C_{25}H_{26}Cl_7N_4$.	I.	II.	Found. III.	IV.
C	57.32	57.47	57.54		
H	4.56	4.54	4.60		
Cl	31.00	···	···	30.96	31.03

The compound forms concentric groups of long lemon-colored
needles that melt at 227°–229°, but begin to darken at 210°. It is

insoluble in hot water, benzene and ether, moderately soluble in hot chloroform, readily in glacial acetic acid and hot alcohol, pretty soluble in cold alcohol. Like the preceding compound it is insoluble in acids and alkalies.

It would be useless to speculate on the constitution of these substances until a more detailed investigation of their behavior towards reagents has been made. The research will be continued in this direction, and it is also proposed to examine other anilides, as well as alkyl amides, in a similar manner.

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PRELIMINARY NOTES.

By Arthur Michael.

The approaching close of laboratory work for the present college year finds myself and co-workers with a number of unfinished investigations. It was thought advisable to state briefly the principal results that we have obtained, before the publication of the papers in full.

I. About five years ago Bischoff and Emmert[1] examined the action of bromine on propenyl-tricarboxylic acid, and obtained, besides other compounds, a dibrompyrotartaric acid that is isomeric with the three acids obtained by addition of bromine to ita-, citra- and mesaconic acids. The discoverers do not attempt to give a constitutional formula to this interesting acid ; but, keeping the behavior of malonic acid and its derivatives towards bromine in mind, there can be no doubt that the reaction is represented by the following equation:

$$CH_3 - CH - COOH \qquad CH_3 - CH - COOH$$
$$CH{<}^{COOH}_{COOH} + 2Br_2 = \qquad CBr_2 - COOH.$$
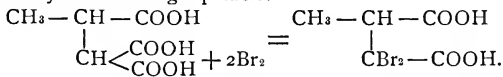
This interpretation is corroborated by the fact that α-bromcrotonic acid was found among the products of the reaction :[2]

$$CH_3 - CH - COOH$$
$$CBr_2 - COOH =$$
$$\qquad CH_3 - CH - CBr - COOH + HBr + CO_2.$$
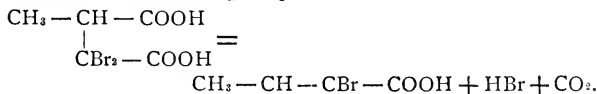
[1] Berichte **15**, 1107.   [2]*Ibid.* **14**, 616.

This explanation of the reaction made it very probable that the third possible dibromsuccinic acid would be obtained by the action of bromine on ethenyl-tricarboxylic acid:

$$\begin{matrix} CH - (COOH)_2 \\ | \\ CH_2 - COOH \end{matrix} + 2Br_2 = \begin{matrix} CBr_2 - COOH \\ | \\ CH_2 - COOH \end{matrix} + CO_2 + 2HBr.$$
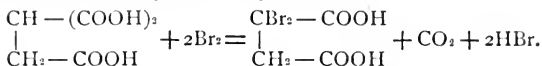
I have made a number of experiments by heating bromine and the acid in a sealed tube at 100°, and have obtained a dibromsuccinic acid which in its properties very closely resembles the symmetrical dibromsuccinic acid obtained by addition of bromine to maleic acid. However, it is extremely probable that the unsymmetrical acid would pass over into the symmetrical compound when exposed to the conditions of the experiment, and I shall repeat the experiments except that the substances will be allowed to act in the cold, which were the conditions that gave the unsymmetrical dibrompyrotartaric acid.

II. It is customary in examining the reactions of guanidine to use the carbonate, but I have found that an alcoholic solution of guanidine sulphocyanate and sodium ethylate acts as free guanidine, and gives the reactions in a much more satisfactory manner. Thus, by treating this solution in the cold with phenyl-mustard oil or benzile, the compounds described by Bamberger[1] and Wense[2] are obtained in almost theoretical yield. The solution gives reactions that cannot be realised with the carbonate. As an instance, it unites with phthalic anhydride to form the compound $C_6H_4{<}{\begin{matrix} COOH \\ CO - NH - C \end{matrix}}{\begin{matrix} -NH_2 \\ -NH \end{matrix}}$ which crystallises in large prisms and melts at 202°. Of greater interest is the action of cyanogen on the solution. Two compounds are formed in the reaction, one crystallising in long needles, and the other in indistinct yellow crystals that are somewhat soluble in water, giving the solution a beautiful fluorescence that is very nearly like that caused by resocyanine. The formula of this substance is $(C_1N_1O_1H_2)_x$, but it is evidently of very complicated composition.[3]

III. With Mr. G. M. Browne, the reactions of guanidine have

[1] Berichte der deutschen chemischen Gesellschaft **13**, 1580.   [2] *Ibid.* **19**, 761.

[3] While working with cyanogen it occurred to me to see whether it would react on alcoholic solutions of sodium acetacetic and sodium malonic ethers, as these substances behave like bases towards many reagents. (This Journal **9**, 124.) I found that a reaction takes place with great readiness, forming crystalline salts. It is my intention to have the reaction further examined.

been further studied. Benzoic ether and an alcoholic solution of guanidine sulphocyanate with sodium ethylate (1 mol. salt to two mols. $NaOC_2H_5$) gives no less than four distinct crystalline products. The reaction is very complicated and its study not yet completed. Guanidine sulphocyanate, sodium ethylate, and malonic ether give a substance crystallising in plates with both acid and basic properties. It has the constitution $NH = C < \frac{NH-CO}{NH-CO} > CH_2 + H_2O$. A. Pinner[1] obtained a condensation product by the action of acetacetic ether on benzenyl-amidine, but was unsuccessful in a similar experiment with malonic ether. Such a product is obtained if an alcoholic solution of sodium malonic ether is used, and the reaction gives results with other bibasic ethers, as oxalic ether, sodium ethyloxide, and the amidine also give a condensation product.

IV. We have also continued our investigation on the isomerism of unsaturated acids. On treating solid crotonic acid, dissolved in carbon bisulphide, with chlorine at a low temperature, $\alpha\beta$-dichlorbutyric acid was obtained. This acid crystallises in prisms that melt at 63°. By treating the acid with alcoholic soda a fourth chlorcrotonic acid is formed, which crystallises in needles and melts at 67°. The acid differs in its properties and in its salts from the three previously known chlorcrotonic acids; and, as is evident from our previous work,[2] has the constitution $CH_3 — CH — CCl — COOH$. It is the alpha-derivative of allocrotonic (isocrotonic) acid. We also made the observation that $\alpha\beta$-dichlorbutyric ether gives α-chlorcrotonic acid (97°) when treated with alkalies, which, in view of the fact that the free acid gives the allo-alphachlorcrotonic acid, is an interesting result.

V. With E. A. de Schweinitz, the action of sodium ethylate on mixtures of amides and ethers was continued. We find that urea, carbonic ether, and sodium ethylate give allophanic ether. From succinic ether, instead of carbonic, the compound

$$CH_2 — CO — NNa — CONH_2$$
$$|$$
$$CH_2 — CO — NNa — CONH_2$$
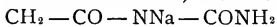
was obtained. Urea sodium ethylate and benzile give $C_6H_5 — CO — \overset{N-CONH_2}{\underset{||}{C}} — C_6H_5$, and from aceta-

[1] Berichte der deutschen chemischen Gesellschaft **18**, 763.

[2] Berichte der deutschen chemischen Gesellschaft **19**, 1378, 1386; **20**, 550; Jr. prkt. Chemie [2] **35**, 257.

mide with oxalic ether acetyloxamic acid was obtained. Organic ethers do not react on compounds as weakly basic as metanitraniline, but a reaction takes place if sodium ethyloxide is present; with oxalic ether the compound $CO - NHC_6H_4NO_2$

$$COOC_2H_5 \text{ was obtained.}$$
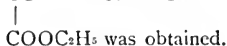
Tufts College, Mass.

A METHOD FOR THE DETERMINATION OF BUTTER IN MILK.

By H. N. Morse and W. M. Burton.

[Second Communication.]

The method for the determination of butter in milk which was described in the preceding number of this Journal,[1] has been subjected to further examination in order to test its accuracy and to ascertain wherein its details could be improved.

The results obtained by a careful comparison indicate that it is quite as accurate as the gravimetric method; while the time required for its execution has been materially shortened by the discovery of the facts:

1st. That a much smaller number of washings with benzine than was formerly prescribed, suffices for the complete extraction of the butter.

2d. That the evaporation of the benzine before saponification is wholly unnecessary.

It has been found advantageous to change in some particulars the mode of procedure in making the determination.

We now begin the grinding of the copper sulphate and milk mixture while the mass is still somewhat moist, since by so doing the labor of reducing it to a fine powder is considerably diminished. Again, when the pulverised material is transferred to the tube for extraction, it is made more compact than formerly by tamping it down from time to time with a glass rod.

The extraction of the butter is effected in the following manner: Fifteen cubic centimeters of benzine are poured over the material

[1] 9, 108.

in the extraction tube and drawn down with the aid of the filter pump until the whole of the mass to be extracted has become wet with the liquid, when the connection with the pump is closed.

After about five minutes another portion of fifteen cubic centimeters of benzine is poured into the tube, and the whole of the liquid slowly drawn through with the aid of the pump into the flask.

As will be shown hereafter, this one extraction suffices in the majority of cases for the complete removal of the butter; nevertheless, for the sake of greater certainty, we are accustomed to wash with three other portions of benzine of 15 cubic centimeters each. The first two or three portions of the benzine are, of course, also used to wash the mortar.

In order to determine the butter thus extracted, the benzine solution, without previous evaporation, is treated with the requisite amount of alkali, and heated for twenty minutes upon the water bath, when the excess of the alkali is determined by means of the standard solution of hydrochloric acid. We have adopted the plan, which, for evident reasons, seems to be the safest, of standardising our solutions by means of the butter extracted by absolute ether from the dried residue of milk.

To prepare them, a solution of potassium hydroxide in 95 per cent. alcohol, slightly stronger than half normal, and a solution of hydrochloric acid containing a little more than 15 milligrams of acid to the cubic centimeter, are made, and the relation of the two to each other carefully determined. The known weight of butter, which has been obtained from the dried residue of 10 cubic centimeters of milk by extracting with absolute ether, evaporating, and drying at 100° to constant weight, is treated with the quantity of the alkaline solution which is equivalent to 25 cubic centimeters of the acid. The flask is then heated for twenty minutes upon the water-bath to the boiling point of the solution. Finally, the excess of the alkali is determined by means of the hydrochloric acid, with use of phenolphthalein as the indicator.

The difference between 25 cubic centimeters of the acid, to which the alkali added to the butter was equivalent, and the number of cubic centimeters of the acid which it is found necessary to use in neutralising the excess of the alkali, is the volume of the acid which is required to neutralise the alkali used up in the saponification of the known weight of butter. The acid is now

so diluted that one cubic centimeter of it will neutralise the alkali required for the saponification of 100 milligrams of butter. The alkali is not diluted ; but, in subsequent work, that quantity of it which is equivalent to 25 cubic centimeters of the standard acid is employed in every saponification. The difference, then, between twenty-five and the number of cubic centimeters of the acid required to neutralise the excess of the alkali, expresses in decimal parts of a gram the weight of the butter found.

Solutions of acid and alkali having one-half the strength of those already described, as will be shown hereafter, can also be employed.

Our experimental work embraces the following points, which will be taken up in the order of their statement :

I. A determination of the rapidity with which the butter is extracted by the benzine.

II. An examination of the question, whether it is necessary to evaporate the benzine before saponification.

III. A comparison of the gravimetric and saponification methods of estimating butter which has been extracted from the dried residue of milk by absolute ether.

IV. A comparison of the new with the gravimetric method.

V. An examination to determine whether more dilute standard solutions than those described give equally satisfactory results.

VI. A determination of the strength of the specimen of acid which had been standardised by butter and employed throughout the work.

VII. An examination to determine whether it is as well to dry the milk by means of anhydrous copper sulphate, as by evaporation, when it is desired to estimate the butter gravimetrically by the extraction method.

I.

To determine the rapidity with which the butter is extracted by benzine when the milk is dried by means of anhydrous copper sulphate, the material in the tube was treated with 15 cubic centimeters. This was then drawn down with the aid of the pump until the liquid had reached the bottom of the tube, when the connection with the pump was closed. After about five minutes, another equal portion of benzine was added and the whole drawn through into the flask. Afterwards, four other portions of benzine

of 15 cubic centimeters each were drawn through the material to be extracted, each being, like the first, collected in a separate flask. These solutions, the first consisting of 30 cubic centimeters, the others of 15 each, are designated as 1st, 2d, 3d, 4th, and 5th extracts. Each was treated with alkali and saponified in the manner which has already been described.

In order to ascertain at the same time whether there is any marked difference, as regards efficiency, between very low boiling benzine and that collected at somewhat higher temperatures, two pairs of determinations were, in each case, made; one with benzine collected between 30° and 45°, and the other between 45° and 60°. The three specimens of milk which were employed are designated by the letters A, B, and C.

The lower boiling benzine was employed in making the determinations 1 and 2 of each series; while 3 and 4 were made with the benzine boiling between 45° and 60°.

A.

1.

1st extract gave   3.61 per cent. of butter.
2d–5th extracts gave 0.00   "   "

2.

1st extract gave   3.61 per cent. of butter.
2d–5th extracts gave 0.00   "   "

3.

1st extract gave   3.57 per cent. of butter.
2d   "   "   0.02   "   "
3d–5th extracts gave 0.00   "   "

4.

1st extract gave   3.64 per cent. of butter.
2d–5th extracts gave 0.00   "   "

Results of the First Series.

1. 3.61 per cent. of butter.
2. 3.61   "   "
3. 3.59   "   "
4. 3.64   "   "

B.

1.

1st extract gave   3.82 per cent. of butter.
2d–5th extracts gave 0.00   "   "

2.

1st extract gave   3.74 per cent. of butter.
2d   "   "   0.09   "   "
3d–5th extracts gave 0.00   "   "

3.

1st extract gave   3.72 per cent. of butter.
2d   "   "   0.09   "   "
3d–5th extracts gave 0.00   "   "

4.

1st extract gave   3.84 per cent. of butter.
2d–5th extracts gave 0.00   "   "

Results of the Second Series.

1. 3.82 per cent. of butter.
2. 3.83   "   "
3. 3.81   "   "
4. 3.84   "   "

C.

1.

1st extract gave   4.36 per cent. of butter.
2d–5th extracts gave 0.00   "   "

2.

1st extract gave   4.36 per cent. of butter.
2d–5th extracts gave 0.00   "   "

3.

1st extract gave   4.27 per cent. of butter.
2d   "   "   0.07   "   "
3d–5th extracts gave 0.00   "   "

4.

1st extract gave   4.19 per cent. of butter.
2d   "   "   0.09   "   "
3d   "   "   0.05   "   "
4th–5th extracts gave 0.00   "   "

Results of the Third Series.

1. 4.36 per cent. of butter.
2. 4.36   "   "
3. 4.34   "   "
4. 4.33   "   "

The results obtained indicate that five extractions by the method described are more than sufficient to extract all of the butter, and that benzine boiling between 45° and 60° is nearly, if not quite, as efficient as that collected at lower temperatures. We have made no experiments with benzine collected at temperatures above 60°.

II.

In order to determine whether it is necessary to evaporate the benzine before adding the alkali for the purpose of saponifying the butter, six parallel determinations were made. The benzine in two cases was completely evaporated; in two others it was reduced to one-half of its original volume; while in the case of the third pair the alkali was added to the solution of butter without previous evaporation. The results were:

I.	II.
3.53 per cent. of butter.	3.54 per cent. of butter.
3.52 " "	3.53 " "

III.

3.54 per cent. of butter.
3.52   "   "

The presence of the benzine does not appear to retard the saponification of the butter; and the little which remains in the flask after heating for 20 minutes upon the water-bath does not obscure the end-reaction when the excess of the alkali is determined by means of the standard acid.

III.

To test the agreement between the results obtained by the gravimetric method and those obtained by saponification with the use of solutions which had been standardised by the butter extracted from milk, we have made, in all, twenty-two parallel determinations, employing for the purpose thirteen different specimens of milk, which are designated in the following statement of results by the letters A, B, C, etc.

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The first column contains the results obtained by the gravi-
metric method ; the second, those obtained by the saponification
of the same.

	I.	II.	I.	II.
A.	3.67 per cent.	3.69 per cent.	F. 4.05 per cent.	4.01 per cent.
	3.70	3.67	4.03	4.00
	3.68	3.64	G. 3.59	3.59
B.	3.63	3.62	3.57	3.59
	3.68	3.64	H. 3.35	3.38
	3.65	3.65	I. 3.17	3.18
C.	2.98	2.98	J. 3.37	3.34
	2.99	2.99	K. 3.43	3.40
D.	3.46	3.43	L. 3.65	3.61
	3.44	3.45	M. 3.60	3.59
E.	3.53	3.51		
	3.49	3.50		

The mean of all of the gravimetric determinations is 3.532 per cent.;
while the maximum difference in results in any one of the seven
cases in which more than one estimation was made is 0.05 per cent.
The mean of all of the determinations by saponification is 3.520
per cent. The difference between the mean results by the two
methods is only 0.012 per cent. The maximum difference between
the weights of any one specimen of butter determined by actual
weighing and then by saponification is 0.04 per cent.

It appears, therefore, that the weight of potassium hydroxide
required to saponify a given quantity of butter is very constant.
The considerable variations in the amounts required to decompose
one gram of butter (from 221.5 to 232.4 milligrams), which were
found by Koettstorfer,[1] may have been due, we think, to a fact
which was afterwards pointed out by Medicus and Scherer,[2]
namely, that when butter is fused and allowed to cool without
agitation, a partial separation of the constituents takes place, so
that the composition of the solidified mass is not homogeneous.

IV.

Five series of determinations were made for the purpose of com-
paring the new with the gravimetric method. Each series con-

[1] *Zeitschrift für analytische Chemie* **18**, 199 and 431.   [2] *Ibid.* **19**, 161.

sisted of four estimations by the new, two by the gravimetric method, and a determination by saponification of each of the gravimetric results.

Each of the series is complete, with the exception of the first, in which one of the gravimetric determinations failed in consequence of the breaking of the flask. In this work every extraction and saponification was repeated in order to demonstrate its completeness. Four of the specimens of milk employed were from the same source, but were obtained on different days.

The different series are designated by the letters A, B, C, D, and E.

In column I are placed the results obtained by the gravimetric method; in column II the results of saponifying the same; and in column III the results obtained by the new method.

I.	II.	III.
	A.	
3.35 per cent.	3.38 per cent.	3.40 per cent.
		3.37
		3.41
		3.41
	B.	
2.97 per cent.	2.98 per cent.	2.97 per cent.
2.99	2.98	2.95
		2.97
		2.95
	C.	
3.46 per cent.	3.43 per cent.	3.47 per cent.
3.44	3.45	3.46
		3.46
		3.50
	D.	
3.53 per cent.	3.51 per cent.	3.48 per cent.
3.49	3.50	3.52
		3.49
		3.48

E.

4.05 per cent.	4.01 per cent.	3.98 per cent.
4.03	4.00	3.97
		3.98
		3.99

V.

To determine whether it is practicable to employ more dilute standard solutions than those we have described, portions of the acid and alkali were diluted to one-half their strength, so that the alkali was approximately quarter normal, while 1 cubic centimeter of the acid was equivalent to the alkali required to saponify 50 milligrams of butter. Three determinations with the original, stronger solutions, and three with the more dilute, were made.

The results were :

I.	II.
3.32 per cent.	3.34 per cent.
3.36	3.32
3.32	3.32

VI.

It was stated in the preliminary article that the amount of potassium hydroxide required to saponify one gram of butter extracted from milk appeared to be more nearly 230 than 227 milligrams. It seemed desirable, therefore, to determine with great care the strength of the specimen of hydrochloric acid which we had standardised by means of butter, and employed with such satisfactory results throughout our work. This was done by means of two specimens of oxalic acid, the one made from pure sugar, the other extracted from so-called chemically pure acid by cold water and recrystallised ; also by means of pure calcite. Neither specimen of the oxalic acid left any residue on ignition.

A cubic centimeter of our hydrochloric acid, which had been so standardised that one cubic centimeter of it would neutralise the potassium hydroxide required to saponify 100 milligrams of butter, was found to be equivalent to

22.952 milligrams of KOH (according to acid No. 1).
22.949 milligrams of KOH (according to acid No. 2).
22.958 milligrams of KOH (according to the calcite).

The mean of the three results is 22.953 milligrams, which would indicate that the quantity of potassium hydroxide required to saponify one gram of butter extracted from milk is 229.53 milligrams.

Since we now have, in tropaeolin (oo), an indicator which is not affected by carbonic acid, pure calcite is to be recommended as a substance by which to determine the strength of acids and alkalis. The method of using it is simple and the results quite satisfactory.

The pulverised and weighed calcite is treated with an excess of the acid whose strength is to be ascertained, and a few drops of an aqueous or alcoholic solution of tropaeolin. The excess of the acid is then determined by means of an alkali whose relation to the acid is known. If the solutions are colorless, the change in the color of the tropaeolin, from red to light yellow, is sufficiently distinct to enable one to obtain quite exact results.

VII.

Two series of determinations of three each were made, in order to ascertain whether, when it is desired to make a gravimetric estimation of butter in milk by the usual extraction method, it is as well to dry the milk by means of anhydrous copper sulphate as by evaporation.

The results were :

Milk dried by $CuSO_4$.		Milk dried by Evaporation.	
3.67 per cent. of butter.		3.70 per cent. of butter.	
3.63 " "		3.65 " "	
3.65 " "		3.63 " "	

Perhaps this method of drying may also be found useful in dehydrating other materials in which estimations of fat are to be made.

The benzine with which the butter is extracted, the alcohol employed to wash down the sides of the flask during titration, or to dilute the solution of potassium hydroxide, and the water used to dilute the acid to the desired standard, must of course be absolutely neutral, and the testing of the three liquids, especially the alcohol and the water, with phenolphthalein should never be omitted.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

NOTES.

Genesis of the Elements.

Two recent papers[1] by William Crookes, F. R. S., afford a pleasant relief to the usual current of thought in chemical literature. Many a reader of the journals passes very lightly over records of research upon rare elements, feeling that the details of such a field can have little present value either for the practical applications of chemistry or for the development of broad scientific generalisation. The work of Prof. Crookes upon yttrium, however, in which he persevered for years with little hope of reaching a full interpretation of his results, has now borne valuable fruit in the extension of our atomic theory.

The two papers already cited cover the same ground in part and embrace the following points:

1. The nature of the "elements" is open for discussion.

2. The "periodic law" shows that the several elements are closely related as members of one family.

3. Prout's hypothesis suggests an evolution of elements from a simple form of matter; perhaps the "half units" may be explained by the hypothetical "helium."

4. The association in nature of certain groups of similar elements is a remarkable fact which cannot be dismissed by saying that "birds of a feather flock together."

5. Certain compound radicals, as cyanogen, follow the analogy of chemical elements in their behavior. May not our "elements" also be compound radicals in their real nature?

6. Carnelley compares the several groups of our elements to the different series of hydrocarbons, and he even suggests their derivation from two constituents, A and B, whose atomic weights are assumed to be $+12$ and -2.

7. Mills suggests that the elements have been formed during a process of gradual cooling, by successive polimerisation — as I yields I_2, S_2 yields S_6, NO_2 is condensed to N_2O_4, aldehyde is converted into paraldehyde, etc., with evolution of heat.

8. Reynolds represents the periodic classification of the elements by the trace of an oscillating pendulum. Crookes modifies this diagram, representing by the ordinates the gradually diminishing temperature of pre-geologic time, and by the abscissas the increasing and diminishing quantivalence of successive elements, which may be associated with varying amounts of electricity. "Protyle" is a name given to the assumed "original primal matter existing before the evolution of the chemical elements."

9. "Each well-defined element" represents conditions of comparative stability. It does not follow that all atoms of the same element are identical in composition and in aggregate weight.

[1] "Address to the Chemical Section of the British Association, 1886." "Genesis of the Elements," a lecture delivered February 18, 1887.

Atoms of Ca, for instance, may vary from 39 to 41, or even through a wider range, the accepted atomic weight being the most common value, and the mean value for all calcium atoms.[1]

10. The phosphorescent spectra of didymium and yttrium sulphates present a series of autograph inscriptions from the molecular world; but the strange language could not be interpreted until a Rosetta stone was found in Marignac's "gadolinia." The spectrum of this earth is similar to that of yttria, but *the characteristic "citron band" is omitted*, and the double green band of samaria is added.

11. By an elaborate system of fractionation (based upon the partial precipitation of a dilute solution of yttrium by ammonia) a series of products was obtained, giving no less than five distinct phosphorescent spectra, but all giving the same incandescent spectrum. Three explanations are possible:

a. That which we call the yttrium atom may have a varying structure, always changing to the same form (that of maximum stability) in the electric spark. Crookes regards this view as the most reasonable.

b. Yttrium may consist of eight or nine different elements, yielding the several bands of the phosphorescent spectra.

c. According to de Boisbaudran, the phosphorescent spectra are due to impurities in the yttria.

12. Nordenskiöld (Compt. rend., Nov. 2, 1886) gives the name gadolinia to the crude mixture of yttria, erbia, ytterbia, etc., just as it is precipitated from the minerals containing these rare earths; and he announces that *this mixture has a constant atomic weight.* These elements, then, always occur together in nature, and always in the *same proportions.* With this new fact the supposed evidence that yttrium is an element vanishes; and the same principle may apply to other "elements." The very idea of an element as something absolutely primary and ultimate seems to be growing less and less distinct.

13. "The figures representing the scale of atomic weights may be supposed to represent inversely the scale of a gigantic pyrometer plunged into a cauldron where the elements of suns and worlds are undergoing formation. As the heat sinks the elements generated increase in density and atomic weight."

14. On the other side of the line is room for Carnelley's element of negative atomic weight. Or, is electricity one of the negative elements and luminiferous ether another?

The author, with the earnest hope that chemistry, like biology, may find its Darwin, looks forward to the day when we may foresee the results of every conceivable reaction, and theories may legitimate themselves by the power of prediction.

<div style="text-align: right;">Robt. B. Warder.</div>

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[1] Such fluctuation of the atomic weight of each element, *within very narrow limits,* would exactly account for the small discrepancies observed between the atomic weights as determined by careful experiment, and a precise application of "Prout's law"; for, if we assume that the weight of each *atom* is an exact multiple of that of hydrogen (or of helium), the *average* atomic weight for each element would vary slightly from a normal value.

Probable Synthesis of one of the Sugars.

Although the carbohydrates are among the best known compounds of carbon, and they have been the subject of numerous investigations, no synthesis of any member of the group has been effected up to the present time. In a paper by E. FISCHER and J. TAFEL, recently published, a reaction is described which apparently yields a member of the sugar group — probably glucose. The work was undertaken with the object of studying the changes which poly-acid alcohols undergo when oxidised. By oxidising glycerin a product was obtained which was shown to be either glycerin aldehyde, $CH_2OH.CHOH.COH$, or the isomeric ketone, $CH_2OH.CO.CH_2OH$. To decide between these two possibilities the attempt was made to prepare the aldehyde of glycerin from acrolein. Bibromacrolein was made and treated with caustic baryta. Thus there was obtained an easily soluble substance which readily reduces Fehling's solution and has all the properties of an aldehyde-alcohol. It was found impossible to get from the solution a crystallised substance. By treating it with phenylhydrazine, however, an *osazone* of the hexane series of the formula $C_{18}H_{22}N_4O_4$ was obtained. The name *osazone* is given to those hydrazine derivatives which are obtained by treating aldehyde alcohols with phenylhydrazine. All these compounds are derivatives of glyoxal-diphenylhydrazine, $\begin{array}{l} HC - N_2H.C_6H_5. \\ HC - N_2HC_6H_5 \end{array}$. Thus the

glycerin derivative which is called phenylglycerosazone is represented by the formula
$$\begin{array}{l} CH_2OH \\ C - N_2H.C_6H_5 \\ HC - N_2H.C_6H_5. \end{array}$$
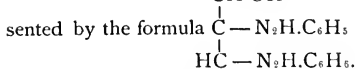
In an earlier paper E. Fischer and A. Steche showed that the action of phenylhydrazine on dextrose and on levulose takes place as represented in the equations :

1. $C_6H_{12}O_6 + C_6H_5.N_2H_3 = C_6H_{12}O_5.N_2H.C_6H_5 + H_2O$;
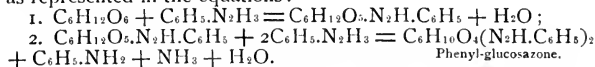
2. $C_6H_{12}O_5.N_2H.C_6H_5 + 2C_6H_5.N_2H_3 = C_6H_{10}O_4(N_2H.C_6H_5)_2 + C_6H_5.NH_2 + NH_3 + H_2O.$ Phenyl-glucosazone.

The product obtained from bibromacrolein shows the greatest resemblance to phenylglucosazone. It melts at exactly the same temperature, and cannot be distinguished from it by its appearance. "Nevertheless," say the authors, "in view of the importance of the question we hesitate to assert their identity, and leave the decision to future experiments. This much, however, appears to us to be beyond question, that the described osazone belongs to a member of the sugar group which is formed from bibromacrolein by treatment with barium hydroxide, as represented in this equation :
$$2C_3H_4Br_2O + 2Ba(OH)_2 = C_6H_{12}O_6 + 2BaBr_2.$$
We shall, as a matter of course, repeat these experiments on a larger scale and later discuss the process in detail."—(*Berichte der deutschen chemischen Gesellschaft* **20**, 1088.)   I. R.
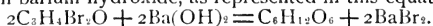
AMERICAN

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ON THE ANILIDES OF FUMARIC AND MALEIC ACIDS AND ON PHENYLASPARTIC ACID.[1]

By Richard Anschütz and Quirin Wirtz.

In the course of comparative researches, which have extended over a long period in this laboratory, on fumaric and maleic acids, itaconic, mesaconic and citraconic acids, O. Strecker prepared the amides and anilides of the three last-mentioned acids.[2] The investigation of the amides and anilides of fumaric and maleic acids ought to be pursued in connection with that of the transformation of both acid chlorides. The serious difficulties, however, which we have thus far encountered in attempts to obtain the chloride of maleic acid in a state of purity have prevented our efforts being crowned with success. If, notwithstanding this, we communicate our experience with the anilides of both acids, we are compelled to take this step on account of the extensive investigations which Michael has for some time been carrying on in the same field, the results of which do not harmonize with our observations. We will therefore give our results obtained in studying the anilides of fumaric and maleic acids together with the analytical proofs, and then compare the same with those of Michael and Wing[3] as well as those of Michael and Palmer.[4]

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CH.CONH.C₆H₅

Fumaric dianilide, $\begin{array}{c} \text{CH.CONH.C}_6\text{H}_5 \\ \| \\ \text{CH.CONH.C}_6\text{H}_5 \end{array}$ —We prepared this com-

pound by gradually mixing an ethereal solution of aniline and an ethereal solution of fumaryl chloride. On treatment with water, in which the fumaric dianilide is insoluble, it is separated from the aniline hydrochloride, which is also formed during the reaction. The dianilide is almost insoluble in ether, very difficultly soluble in alcohol and in glacial acetic acid. It crystallises from the latter in white microscopic needles, which turn brown at 275° without melting. When heated with a concentrated solution of alcoholic potash in a closed tube by means of a water-bath, the fumaric dianilide is decomposed into aniline and fumaric acid.

I. 0.1713 gram substance burned with chromate of lead gave 0.4490 gram CO_2 and 0.0867 gram H_2O.

II. 0.1946 gram substance burned in open tube gave 0.5124 gram CO_2 and 0.0999 gram H_2O.

III. 0.1397 gram substance burned in open tube gave 0.3678 gram CO_2 and 0.0696 gram H_2O.

IV. 0.3682 gram substance gave 34.6 cc. N at 24° and under 753.5 mm. pressure.

	Theory for $C_{16}H_{14}N_2O_2$.	I.	II.	III.	IV.
		Found.
C	72.18	71.50	71.81	71.80	...
H	5.26	5.62	5.70	5.53	...
N	10.52	...	...	...	10.44
O	12.03	...	...	...	...
	99.99

Bromine addition product of fumaric dianilide, $C_2H_2Br_2$ ($(CONHC_6H_5)_2$.—The fumaric dianilide unites with two atoms of bromine, and is thereby in all probability changed into the anilide of ordinary dibromsuccinic acid. If a solution of fumaric dianilide in glacial acetic acid be treated with the theoretical amount of bromine and heated to 100° in a closed tube till the color of the bromine has disappeared, the addition product is obtained as a white powder, which does not melt even at 100°.

0.1943 gram substance gave 0.1708 gram AgBr.

	Theory for $C_{16}H_{14}Br_2O_2N_2$.	Found.
Br	37.55	37.41

We shall attempt to prepare the anilide of ordinary dibrom-succinic acid directly from its chloride, in order to compare it with the bromine addition product of fumaric dianilide.

The substance, which Michael and Wing recently stated to be fumaric dianilide, is entirely different from the fumaric dianilide obtained by us from fumaryl chloride and aniline. The above-named chemists observed, during the gradual heating of mono-aniline malate to 230°–250°, the formation of a yellow substance crystallising in needles which, after several recrystallisations from water, melted at 87.5°. Its analysis gave figures agreeing with the formula for fumaric dianilide. The results of the analyses, together with the fact that this compound was totally different from one of like composition which melts at 211°, and which is formed from maleic acid and aniline, very likely led Michael and Wing to the assertion that the compound melting at 87.5° was apparently fumaric dianilide.

Owing to these unintelligible contradictions we have repeated the distillation of monoaniline malate.

Monoaniline malate, $COOH.CH_2.CHOH.COOH.NH_2C_6H_5$.— The aniline salt of malic acid is, like the ammonium salt, easy to prepare in a crystalline condition. The assumption that the aniline unites with that carboxyl which is in combination with the CHOH group, and not with the other carboxyl, appears to be justified. The monoaniline malate is conveniently prepared by treating an alcoholic solution of malic acid with aniline. The employment of 21 grams aniline and 30 grams malic acid gave 47 grams of the salt after the first crystallisation, while the theoretical yield is only 51 grams. The monoaniline malate consists of small white prisms melting at 143°–144°.

I. 0.1793 gram substance gave 0.3481 gram CO_2 and 0.1014 gram H_2O.

II. 0.1673 gram substance gave 0.3240 gram CO_2 and 0.0905 gram H_2O.

III. 0.1619 gram substance gave 0.3127 gram CO_2 and 0.0893 gram H_2O.

	Theory for		I.	Found. II.	III.
	$C_{16}H_{20}N_2O_5$.	$C_{10}H_{13}NO_5$.			
C	58.18	52.85	52.95	52.82	52.67
H	6.06	5.74	6.28	6.01	6.13
N	8.48	6.18	...	...	...
O	27.27	35.23	...	...	...

Distillation of monoaniline malate.—On subjecting monoaniline malate to distillation under ordinary pressure, the operation being conducted in a small retort placed in a graphite bath, water and aniline first go over, then yellow needles sublime, and later the portion which distills solidifies to a yellowish-white mass. A black viscous substance finally remains in the retort. The monoaniline malate gives a greater yield of the distillate by being first heated to 230°, then subjected to distillation under diminished pressure. 50 grams monoaniline malate gave 31 grams solid distillate. On treatment of the distillate with alcohol, the yellow substance goes into solution, while by far the greater part of the solid mass remains as a brown powder. That portion which was difficultly soluble in alcohol proved to be the so-called *maleic dianilide*, with the melting point 211°. After one recrystallisation from glacial acetic acid it gave the following figures :

I. 0.1729 gram substance gave 0.4543 gram CO_2 and 0.0894 gram H_2O.

II. 0.3870 gram substance gave 36.5 cc. N at 9.7° under 761.5 mm. pressure.

	Theory for $C_{16}H_{14}O_2N_2$.	Found.	
		I.	II.
C	72.18	71.66	...
H	5.26	5.74	...
O	12.03	...	...
N	10.52	...	11.35

The solid substance remaining after extraction with alcohol contained, besides a little maleic dianilide, the yellow-colored compound, which was extracted with benzene and precipitated with naphtha. After being several times dissolved in benzene and precipitated with naphtha it was obtained in a pure condition. The results of its analysis as well as its behavior prove this substance to be *maleinanil*.

Maleinanil, $C_2H_2(CO)_2N.C_6H_5$, melts, after several recrystallisations from low-boiling naphtha to which a little benzene is added, at 90°-91°, and consists of long yellow needles. It is easily soluble in benzene, chloroform, ether, and alcohol, difficultly soluble in carbon disulphide and low-boiling naphtha. On gradually cooling a solution of maleinanil in hot water, in which it is difficultly soluble, long yellow and often curved needles separate. The manner in which maleinanil crystallises from water reminds one of citraconanil.

One of us (A.), conjointly with W. O. Emery, determined the boiling point of maleinanil and of citraconanil under greatly diminished pressure.

Maleinanil boils at 162.1°–162.3° under 12 mm. pressure (temperature of paraffin bath 179°).

Citraconanil boils at 171.7° under 12 mm. pressure (temperature of paraffin bath 190°).

I. 0.2005 gram substance burned with lead chromate gave 0.5120 gram CO_2 and 0.0831 gram H_2O.

II. 0.1795 gram substance gave 0.4555 gram CO_2 and 0.0729 gram H_2O.

III. 0.3625 gram substance gave 25.8 cc. N at 10.5° and 767 mm.

IV. 0.3694 gram substance gave 24.3 cc. N at 4.7° and 759 mm.

	Theory for $C_{10}H_7O_2N$.	Found.			
		I.	II.	III.	IV.
C	69.37	69.64	69.21	...	...
H	4.04	4.60	4.51	...	...
O	18.49	...	...	...	...
N	8.09	...	...	8.58	8.04

In order to show the direct relation of maleinanil to maleic acid we treated maleic anhydride with aniline, in the proportion of equal molecules, and distilled the resulting product. Under these conditions the so-called maleic dianilide was the chief product, and it was accompanied by maleinanil, which could easily be detected by the method already mentioned.

Either the maleinanil or the so-called maleic dianilide is the principal product, according to the manner of conducting the distillation of monoaniline malate. The above-cited distillation of 50 grams monoaniline malate gave 31 grams distillate, from which were obtained 18 grams of the so-called dianilide and 7 grams of anil. If, on the other hand, the distillation be conducted under a pressure of 12 mm. and in a paraffin bath heated to 215°, much larger quantities of anil are formed, while the so-called maleic dianilide occurs in relatively smaller quantities. The formation of the latter substance in this decomposition was overlooked by Michael and Wing. The contradiction between their statements and our own, in relation to the properties of fumaric dianilide, has found an explanation in a surprising way. What Michael and Wing believed to be fumaric dianilide is nothing but maleinanil. That our preparation shows the melting point 90°–91°,

instead of 87.5°, perhaps indicates its greater degree of purity. How the different analytical results of Michael and Wing are to be explained we cannot conjecture, since the figures given by the above-named chemists are doubtless distorted through typographical errors. Not only is the percentage of N in $C_{16}H_{14}N_2O_2$ incorrectly stated, but also the percentage of N is incorrectly calculated from the data. We write the figures calculated by us from Michael and Wing's statements in brackets beside those taken from their paper.[1]

"0.2872 gram substance gave 0.7642 gram CO_2 and 0.1262 gram H_2O.

0.1484 gram substance gave 18 cc. N at 21° and 750 mm.

	Theory for $C_2H_2(CONHC_6H_5)_2$.	Found.
C	72.10 (72.18)	72.55 (72.57)
H	5.26 (5.26)	4.86 (4.88)
N	9.82 (10.52)	10.19 (13.63)".

The complete explanation of the constitution of maleinanil, which has one of the following formulas,

$$\text{I.} \quad \begin{array}{l} \text{CH.CN.C}_6\text{H}_5 \\ \| \quad > \text{O} \ ; \\ \text{CH.CO} \end{array} \qquad \text{II.} \quad \begin{array}{l} \text{CH.CO} \\ \| \quad > \text{N.C}_6\text{H}_5, \\ \text{CH.CO} \end{array}$$

will require further experiments.

Dibromsuccinanil, $C_4H_2Br_2O_2NC_6H_5$, is easily prepared by treating a solution of maleinanil in chloroform with bromine. It gives, after recrystallisation from chloroform, white crystalline crusts, melting at 158°–159°.

0.2663 gram substance, heated in a closed tube with concentrated nitric acid, gave 0.3051 gram AgBr.

	Theory for $C_{10}H_7O_2Br_2N$.	Found.
Br	48.05	48.75

$$\begin{array}{l} \text{CH.CONC}_6\text{H}_5 \\ \text{Fumaranilic acid,} \quad \| \\ \text{CH.COOH} \end{array} \quad .\text{—By this name we indicate}$$

the anilic acid obtained by careful treatment of maleinanil with alkalies, since by the energetic action of alkalies it is converted into fumaric acid.[2]

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[1] See note by Michael, this Journal **9,** 184.—Ed.

[2] This astonishing fact forms at first sight one of the arguments by means of which I seek in the following paper, "On the Isomerism of Fumaric and Maleic Acids," to establish my opinion regarding this kind of isomerism, and it will therefore be further discussed in the proper place.

Maleinanil, like citraconanil, dissolves readily in ammonia by gentle warming. By means of hydrochloric acid a precipitate is obtained from this solution which, after being several times dissolved and precipitated, gave the melting point 183°–184°. As the analysis of this product always gave too high a percentage of carbon, we substituted for ammonia barium hydrate solution, according to the method of Menschutkin.[1]

In this reaction too high a temperature must not be used, nor must the heating be continued too long, lest the decomposition go too far, in which case great loss of fumaranilic acid would result. In order to retain the carbonic acid the maleinanil is warmed to 30°–40° in a closed tube with a slight excess of a solution of barium hydrate, its solution being aided by frequent and violent shaking. If the mixture be heated for a time at 100°, considerable quantities of monobarium fumarate separate. The solution of the barium salt is next saturated with carbon dioxide to free it from excess of barium hydroxide, the barium carbonate separated by filtration, after which the fumaranilic acid is precipitated in the cold with hydrochloric acid. After several recrystallisations from alcohol the fumaranilic acid is obtained in prisms of a faint yellow color. These melt at 187°–187.5°, and are difficultly soluble in water.

I. 0.1689 gram substance burned with lead chromate gave 0.3873 gram CO_2 and 0.0734 gram H_2O.

II. 0.1360 gram substance gave 0.3122 gram CO_2 and 0.0592 gram H_2O.

III. 0.3954 gram substance gave 24.6 cc. N at 4.5° and 762 mm.

	Theory for $C_{10}H_9NO_3$.	Found.		
		I.	II.	III.
C	62.82	62.54	62.60	…
H	4.71	4.82	4.83	…
N	7.33	…	…	7.64
O	25.13	…	…	…

Upon heating the fumaranilic acid with a slight excess of a concentrated solution of alcoholic potash in a closed tube, potassium fumarate separates after a short time. After filtration the salt is dissolved in water, then acidified with hydrochloric acid, when pure fumaric acid is obtained. Although we were convinced that we had obtained fumaric acid by its conduct on heating, its

[1] Annalen der Chemie **162**, 176.

difficult solubility in water and the insolubility of its barium salt, we nevertheless analysed the free acid.

0.1752 gram substance gave 0.2667 gram CO_2 and 0.0592 gram H_2O.

	Theory for $C_4H_4O_4$.	Found.
C	41.38	41.51
H	3.45	3.74
O	55.17	...

After these results it was especially interesting for us to compare the maleinanilic acid with the fumaranilic acid obtained from maleinanil. Michael and Palmer make only a brief statement concerning the maleinanilic acid, which, however, does not at all agree with our own experience. According to Michael and Palmer the maleinanilic acid is formed in the following manner : " If a solution of one part maleic acid in ten parts of water be treated with enough aniline to form the acid salt, and if this solution be allowed to stand for a few days, the gradual separation of a crystalline substance is observed, which, after recrystallisation from alcohol, consists of prisms melting at 207°. This compound has the constitution $C_2H_2 \big\langle {}^{CO.NHC_6H_5}_{COOH}$. It is readily soluble in alkalies, but insoluble in hydrochloric acid." This reaction has already been studied by W. H. Perkin,[1] who first investigated the behavior of fumaric and maleic acids towards aniline, and has made the following communication : " If a solution of aniline maleate be evaporated to dryness and the residue be allowed to stand for some time, it becomes entirely insoluble in water, and gives a product which crystallises from alcohol in beautiful needles, melting at 210°–211°. This compound is probably analogous to citraconanil."

" If a saturated solution of aniline maleate be allowed to stand some time in the cold, a crystalline substance separates, which is, however, different from that just described, and is soluble in hot water."

The product, first mentioned by Perkin, is doubtless identical with that which we obtained, together with maleinanil, by distilling monoaniline malate, and is also identical with the compound which Michael believed to be maleic dianilide. We shall show later that both these views are incorrect, and that the substance in question must be regarded as the anil of phenylaspartic acid.

But first we will turn our attention to a description of our experience in investigating the spontaneous decomposition of aniline maleate in a water solution. Our researches in this direction are, however, not yet completed.

Change of Aniline Maleate in Water Solution.

Monoaniline maleate, obtained by mixing a warm concentrated solution of maleic acid with the theoretical amount of aniline, crystallises in large transparent prisms, which, according to the analyses, contain half a molecule of water of crystallisation.

I. 0.2525 gram substance burned with lead chromate gave 0.5066 CO_2 and 0.1206 gram H_2O.

II. 0.2474 gram substance gave 0.4955 gram CO_2 and 0.1235 gram H_2O.

	Theory for		Found.	
	$C_{10}H_{11}O_4N.$	$C_{10}H_{11}O_4N + \frac{1}{2}H_2O.$	I.	II.
C	57.41	55.05	54.71	54.62
H	5.26	5.51	5.30	5.54
O	30.62	33.02	...	...
N	6.70	6.42	...	...

On dissolving the pure and readily soluble salt in a small quantity of water at the ordinary temperature, and allowing the solution to stand, a yellowish-white or often light brown crystalline mass separates, which, though amorphous, is apparently homogeneous. It became evident, however, in an attempt to determine the melting point, that we had a mixture, since the substance began to soften at 130°, melted partially on further heating, without, however, becoming completely liquid at 210°. We find ourselves in contradiction with Michael and Palmer as regards the melting point, and also as regards their statement that the transformation product is insoluble in alkalies and acids.

We have studied the gradual formation of this difficultly soluble substance by means of the balance, and we give some of our observations.

36 grams monoaniline maleate dissolved in somewhat more than 50 cc. H_2O gave:

1. Portion after 24 hours, 0.6 gram.
2.   "   " 24 " 0.67 "
3.   "   " 24 " 0.91 "
4.   "   " 24 " 0.50 "

5. Portion after 48 hours, 2.00 gram.
6.   "   " 48   "   3.00   "
7.   "   " 48   "   3.00   " etc.

At first there were found, together with the amorphous products of transformation, crystals of unchanged monoaniline maleate, which, before filtration, were dissolved by gently warming the solution. The separated mass was often more or less brown in color. A series of combustions of the washed and dried substance was made, the results of two of which we give, as the substance here employed was remarkably pure and homogeneous.

I. 0 2004 gram substance burned with lead chromate gave 0.4146 gram CO_2 and 0.0987 gram H_2O.

II. 0.2147 gram substance gave 0.4480 gram CO_2 and 0.1063 gram H_2O.

	\multicolumn{2}{c}{Theory for}	\multicolumn{2}{c}{Found.}
	$C_{10}H_9NO_3$.	$C_{10}H_{11}NO_4$.	I.	II.
C	62.82	57.41	56.42	56.91
H	4.71	5.26	5.47	5.50

The percentages found are quite different from those required by maleinanil; they, however, approach those values required by maleinanil plus one molecule of water; that is, for monoaniline maleate.

In any case, there occur among the transformation products of monoaniline maleate small quantities of phenylaspartic acid, and a derivative of phenylaspartic acid, which will farther on be discussed at length. This led us to think that perhaps the aniline salt of inactive malic acid was formed as an intermediate product. The main part of the transformation product, however, is quite closely related to maleic acid. On treatment with barium hydrate there is formed, together with other barium salts, which have not yet been investigated, a barium salt crystallising in silver-white leaflets, the analyses of which gave figures agreeing with anhydrous barium malate. The crystals were, however, nothing but the barium salt of maleic acid $+ 1 H_2O$.

I. 0.3824 gram substance burned with lead chromate gave 0.2436 gram CO_2 and 0.0561 gram H_2O.

II. 0.1139 gram substance gave 0.0987 gram $BaSO_4$.

III. 0.2265 gram substance gave 0.1958 gram $BaSO_4$.

IV. 0.1544 gram substance gave 0.1330 gram $BaSO_4$.

V. 1.7267 grams substance lost at 100° in a Liebig's drying tube 0.1199 gram H_2O.

	Theory for $C_4H_2O_4$ Ba + 1 Aq.	Found.				
		I.	II.	III.	IV.	V.
C	17.84	17.37	...	...	...	...
H	1.49	1.63	...	...	...	...
O,	29.74	...	...	...	...	...
Ba	50.93	...	50.95	50.82	50.65	...
	100.00					
Aq	6.69	...	...	...	...	6.94

On treatment of the barium salt with sulphuric acid in the proportion of the molecular weights, we obtained without difficulty pure maleic acid, melting at 130°–131°.

Unfortunately we have not as yet been able to separate, by crystallisation, the transformation products of monoaniline maleate. We must therefore reserve for later research the determination of the relation in which the chief product stands to maleic acid.

On treating the last mother-liquors from the barium salts of the transformation products of monoaniline maleate with hydrochloric acid we obtained after a time a small quantity of well-formed crystals. The same crystals are formed when the transformation product is dissolved directly in hydrochloric acid. They appear to be formed in larger quantities when the solution of monoaniline maleate is allowed to stand a long time by itself. We have not as yet investigated their properties. The base of the hydrochloric acid salt is readily soluble in alkalies and alkaline earths. After a consideration of these peculiarities one is led to suspect the presence of an amido acid. Indeed, the analyses of the hydrochloric acid salt as well as those of the free acid ; further, the synthesis of the latter from monobromsuccinic acid and aniline, all indicate the presence of phenylaspartic acid. The hydrochloric acid salt crystallised from water gave analyses agreeing with the following formula for phenylaspartic acid hydrochloride :

$$C_{20}H_{27}N_2O_{10}Cl = [C_2H_3NHC_6H_5.(COOH)_2]_2 + HCl + 2H_2O.$$
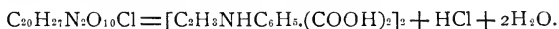
I. 0.2008 gram substance gave 0.3577 gram CO_2 and 0.1043 gram H_2O.

II. 0.2105 gram substance gave 0.3764 gram CO_2 and 0.1080 gram H_2O.

III. 0.2155 gram substance gave 0.0640 gram AgCl.

	Theory for $C_{20}H_{27}N_2O_{10}Cl$.	Found.		
		I.	II.	III.
C	48.91	48.58	48.76	...
H	5.50	5.77	5.70	...
N	5.70	...	...	...
O	32.62	...	...	...
Cl	7.24	...	...	7.34

99.97

As is well known, the amido fatty acids—for example, amido acetic acid—have the property of forming salts with hydrochloric acid, in which two molecules of the amido acid and one molecule of hydrochloric acid occur ; the formula, then, for the hydro-chloride of phenylaspartic acid is not surprising.

Synthesis of Phenylaspartic Acid.

As to prove by means of a breaking down of the substance that it is phenylaspartic acid might be a difficult matter, we attempted to make phenylaspartic acid synthetically from monobromsuccinic acid and aniline.

The monobromsuccinic acid was prepared by treating fumaric acid with a saturated solution of hydrobromic acid in glacial acetic acid.[1] A concentrated water solution of the acid thus obtained was boiled a short time with aniline. On cooling, the phenylaspartic acid gradually separated from the solution. The acid so obtained is by no means pure. Some of the impurities remain behind on treating the crude phenylaspartic acid with hydrochloric acid. The hydrochloride of phenylaspartic acid then separates from the acid filtrate in well-formed crystals, which, after recrystallisation from water, are pure.

I. 0.2092 gram substance burned with lead chromate gave 0.3682 gram CO_2 and 0.1057 gram H_2O.

II. 0.2033 gram substance gave 0.3635 gram CO_2 and 0.1061 gram H_2O.

III. 0.2600 gram substance gave 0.0788 gram AgCl.

IV. 0.1664 gram substance gave 0.0485 gram AgCl.

V. 0.2128 gram substance gave 0.0626 gram AgCl.

[1] Berichte der deutschen chemischen Gesellschaft **11**, 1221.

	Theory for $C_{20}H_{27}N_2O_{10}Cl.$	Found.				
		I.	II.	III.	IV.	V.
C	48.91	48.00	48.76	...	...	...
H	5.50	5.60	5.79	...	...	...
N	5.70	...	...	...	...	...
O	32.62	...	...	...	...	...
Cl	7.24	...	...	7.49	7.21	7.27
	99.97					

The hydrochloride of phenylaspartic acid from monobrom-succinic acid and aniline has therefore the same composition as the phenylaspartic acid hydrochloride obtained from monoaniline maleate. The proof of the identity of both phenylaspartic acid hydrochlorides from different sources is most effectually furnished by the crystallographic evidence, for which we are indebted to Professor Dr. Hintze, who has made a study of the crystals in the Institute of the University of Breslau. He says:

" The monosymmetrical crystals are combinations of prism p (110) ∞P and base c (001) oP, the acute prism-angle being bisected by the plane of symmetry. Although the crystals are bright, still the planes are curved and broken, therefore unsuited for exact measurements. Still, there can be no doubt as to the identity of the several crystallisations of the compound, the one a from monobromsuccinic acid and aniline, the other β from mono-aniline maleate. The measurements made by G. Laird in the Mineralogical Institute of Breslau gave different results for different crystals:

$$\begin{array}{ccc} & a. & \beta. \\ \text{for } p:p = 110:1\bar{1}0, & 53°30'-55° & 54°-55°30' \\ \text{for } p:c = 110:001, & 96°30'-97°30' & 96°-97°20' \end{array} \Big\} \text{Plane angle.}$$

" An average of the best measurements :

$$p:p = 110:1\bar{1}0 = 54°50'$$
$$p:c = 110:001 = 96°50'$$

gives the ratio of the axes :

$$a:b = 1.9957:1$$
$$\beta = 75° 1.5'.$$

" The base is often inclined to a positive hemidoma. Distinct cleavage in the direction (100) $\infty P\infty$. The direction of extinction on the planes of the prism forms with the vertical edge of the prism an angle of about 35°."

Phenylaspartic acid, $C_2H_3NH.C_6H_5(COOH)_2$.—On treating a known weight of phenylaspartic acid hydrochloride with the theoretical quantity of moist silver hydrate, filtering from the silver chloride and evaporating the filtrate in a vacuum desiccator, white masses of phenylaspartic acid gradually separate from the solution. If a solution of phenylaspartic acid be allowed to crystallise slowly, small crystals are formed, which we hope to obtain later in a form suitable for crystallographic measurements.

I. 0.1139 gram substance burned with chromate of lead gave 0.2401 gram CO_2 and 0.0564 gram H_2O.

II. 0.2282 gram substance gave 0.4815 gram CO_2 and 0.1093 gram H_2O.

III. 0.4185 gram substance gave 23.2 cc. N at 4.5° and 772 mm.

	Theory for $C_{10}H_{11}O_4N$.	I.	II.	III.
			Found.	
C	57.41	57.49	57.54	...
H	5.26	5.50	5.32	...
N	6.70	...	...	6.90
O	30.62	...	...	...
	99.99			

The pure phenylaspartic acid melts without decomposition at 131°–132°; acquires, however, at 121° a doughy consistency.

Phenylaspartanil, $C_2H_3NH.C_6H_5.C_2O_2NC_6H_5$.—In describing the distillation of monoaniline malate we have already stated that, besides the maleinanil as the chief product, a substance was formed which is evidently identical with that obtained by Michael and called by him maleic dianilide. As has already been stated, this substance is also formed by heating maleic anhydride with aniline ; at the same time a little maleinanil is formed. In closing the description of fumaric acid anil we took the opportunity of stating that W. H. Perkin had already, in 1881, made researches on the action of aniline upon fumaric and maleic acids, and had also observed the formation from maleic acid of a compound melting at 210°–211°. He regarded this compound as maleinanil, in the belief that it corresponded to citraconanil. At that time Perkin called attention to the fact that aniline fumarate and mesaconate gave no products insoluble in water on evaporating their solutions ; while, on concentrating a solution of citraconate of

aniline, citraconanil was formed. Michael seems to have overlooked this statement of Perkin.[1]

After the foregoing, it is hardly necessary that special reference be made to the contradictions in the statements of W. H. Perkin and of Michael concerning the substance melting at 210°–211°.

We repeated the experiment of Michael, and obtained from 5 grams maleic acid, 0.9 gram of a crude product insoluble in water and melting at 195°–199°. After recrystallisation from alcohol the correct melting point, 211°, was observed.

I. 0.1864 gram substance burned with lead chromate gave 0.4920 gram CO_2 and 0.0870 gram H_2O.

II. 0.1635 gram substance gave 0.4326 gram CO_2 and 0.0801 gram H_2O.

	Theory for $C_{16}H_{14}N_2O_2$.	I.	II.
		Found.	
C	72.18	71.97	72.16
H	5.26	5.18	5.44
N	10.52	...	...
O	12.03	...	...
	99.99		

The analyses prove that the compound obtained from maleic acid and aniline is not maleinanil, but is isomeric with fumaric dianilide described above. The nature of the substance was shown by its decomposition at 100° in a closed tube with alcoholic potash.

Instead of the potassium salt of maleic acid, the formation of which would naturally be expected from maleic dianilide, the potassium salt of phenylaspartic acid was obtained, which, on treatment with hydrochloric acid, gave phenylaspartic acid hydrochloride. The splitting off of the aniline residue is more easily effected if the substance be heated at 100° with fuming hydrochloric acid instead of potassium hydrate. After concentration in a vacuum the phenylaspartic acid hydrochloride crystallises out.

I. 0.1984 gram substance gave 0.3563 gram CO_2 and 0.1033 gram H_2O.

II. 0.2317 gram substance gave 0.0636 gram AgCl.

III. 0.1625 gram substance gave 0.0448 gram AgCl.

	Theory for $C_{20}H_{27}O_{16}N_2Cl$	Found.		
		I.	II.	III.
C	48.93	48.97	...	...
H	5.50	5.78	...	...
O	32.62	...	...	...
N	5.71	...	...	...
Cl	7.24	...	6.80	6.84
	100.00			

The substance melting at 210°–211° is therefore to be regarded as phenylaspartanil, and must be represented by one of the three following formulas:
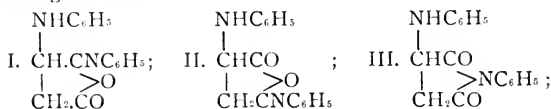
but which of the three is the correct one we are as yet not in a position to decide.

The easily prepared phenylaspartanil forms the most convenient material from which to prepare phenylaspartic acid; moreover, this acid, together with its dianilide, was obtained by Piutti[1] by heating powdered asparagine with dry aniline. He gives as the melting point of phenylaspartanil 209°. From this anil the phenylaspartic acid was obtained; but Piutti did not carry his researches farther than its formation. The formation of phenylaspartic acid from maleic acid and aniline may be explained in different ways.

The question is, Does the aniline unite directly with the maleic acid, or is the maleic acid, by union with water in the presence of aniline, first converted into monoaniline malate, from which, by the splitting off of water, phenylaspartic acid is formed; or have we in the formation of phenylaspartic acid an example similar to that of the transformation of unsaturated acids into γ-lactones; for example, that of pyroterebic acid into isocaprolactone?

The formation of phenylaspartic acid from maleic acid and aniline speaks in favor of the above-mentioned possibilities. On heating equal molecular weights of maleinanil and aniline for a time in a closed tube at 100°, the yellow solution is gradually changed

into a solid white substance having all the peculiarities of phenyl-aspartanil prepared in other ways.

Whether the formation of phenylaspartanil by boiling a solution of monoaniline maleate, or by heating maleic anhydride with aniline, or, further, from monoaniline malate, takes place after the formation, first of maleinanil, then of phenylaspartic acid, or *vice versa*, we are not as yet in a position to decide.

The formation of phenylaspartanil is, in a certain sense, analogous to the formation of aldehyde ammonia, in which case the ammonia breaks the double bond existing between carbon and oxygen, and unites with the aldehyde ; exactly in the same way the addition of maleinanil results after the double bond between the carbon atoms has been broken.

To the best of our knowledge, this breaking of the double bond between carbon atoms by aniline is the first example of such a reaction, the generalisation of which we wish to reserve for further research.

The results of the investigation are, briefly : From fumaryl chloride and aniline, fumaric dianilide is formed, which, on treatment with an alcoholic solution of potassium hydrate, gives fumaric acid. The supposed dianilide of maleic acid has been proved to be phenylaspartanil.

We obtained phenylaspartic acid :

1. From monoaniline maleate.

2. From its anil.

3. From monobromsuccinic acid and aniline.

The anil of phenylaspartic acid is formed :

1. From aniline maleate (boiling of its water solution).

2. By heating :

    a. Maleic acid and aniline.

    b. Maleic anhydride and aniline.

    c. Monoaniline malate.

    d. Maleinanil and aniline.

In both the reactions 2 *b* and 2 *c* there is formed, besides phenylaspartanil, maleinanil, which has been regarded as fumaric dianilide. We converted maleinanil into fumaranilic acid, and this in turn into fumaric acid.

Whether the maleinanil is the chief transformation product when a water solution of monoaniline maleate is allowed to stand for a time must be decided by further investigations.

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It follows from the foregoing comparison that the study of the anilides of fumaric and maleic acids is, in many directions, incomplete. Researches originally planned have not yet been undertaken; new problems present themselves, owing to the unexpected results of some of the reactions. In consideration of these results, the anils and anilides of all the dicarbon acids standing in theoretical relation to fumaric and maleic acids require a new investigation, as a check to that already carried out. The change undergone by monoaniline maleate in water solution needs, first of all, a careful research, which will necessarily occupy us for some time.

We propose to include in the circle of our investigations the amides and imides of fumaric, maleic, and malic acids. For, without doubt, the question concerning the constitution of the so-called fumarimide stands in the closest relation to these problems. This compound is formed by heating ammonium malate, and is readily convertible into inactive aspartic acid.[1]

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[1] The assertion of Michael and Wing that fumaramide is not a fumaric acid derivative is certainly correct, but not entirely new. Kekulé, in 1867, in Vol. II of his Lehrbuch, invariably speaks of fumarimide as the "so-called fumarimide" (see pp. 179-81). At that time structural formulas were not employed in the sense now used, but "typical formulas," which can, however, as Ladenburg has already done (compare Vortraege ueber die Entwickelungsgeschichte der Chemie, 2d edition, p. 278), be converted into modern structural formulas by the aid of the so-called "graphical formulas" to be found in Kekulé's Lehrbuch. From the observations of Kekulé, it is quite evident that he regarded the alcoholic hydroxyl group as participating in the formation of fumarimide, and if the formula given by him for the so-called fumarimide be translated into the language of our modern formulas, the following structural formula is obtained:

$$CO$$
$$CH \!\!-\!\!\!\!\longrightarrow N$$
$$CH_2$$
$$CO$$

The structural formula of fumarimide as expressed by Michael and Wing is introduced in Roscoe and Schorlemmer's Manual of Chemistry (Vol. III, p. 812, 1884) as follows:

$$CO - N - CO$$
$$CH - \quad CH_2$$
$$CH_2 \quad - CH$$
$$CO - N - CO$$
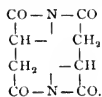
This formula is also intended to represent the change of the so-called fumarimide into aspartic acid. But the constitution of fumarimide is still entirely doubtful, and it is therefore difficult to understand why Michael and Wing desire to abandon the name fumarimide before we really know what kind of a substance is to be understood by this name.—R. ANSCHUTZ.

CONCERNING THE ISOMERISM OF FUMARIC AND MALEIC ACIDS.[1]

By Richard Anschütz.

That kind of isomerism which is observed between fumaric and maleic acids is gradually acquiring more significance since a large number of organic compounds have begun to be classed in the same category, partly with and partly without grounds for such classification. The apparent simplicity of the composition of fumaric and maleic acids, their close relationship to many organic compounds of known constitution, the remarkable changes of both acids and some of their derivatives into one another, the intimate relation to the isomeric malic acids, to the tartaric acids and to the compounds of the furfuran group, make the discovery of a satisfactory explanation, supported by experiments, of the isomerism of fumaric and maleic acids a problem, the solution of which promises to be of fundamental importance to organic chemistry. Before I present my views on this subject it will not be out of place to summarise the most important hypotheses already proposed having for their object the explanation of the isomerism of fumaric and maleic acids, and, secondly, to discuss these hypotheses.

These can be divided into two classes: 1. Those in which it is assumed that the molecule of one acid is twice as large as that of the other; 2. Those in which it is assumed that both have the same molecular weight.

As early as 1838 Liebig[2] in the first of his classical memoirs "On the Constitution of Organic Acids" expressed himself as follows concerning the relation between fumaric and maleic acids: "It is possible that equisitic acid [the name then used for maleic acid] is $C_8H_4O_6 + 2Aq$, and fumaric acid $C_4H_2O_3 + Aq$, that is, that the transformation of one into the other takes place in a manner similar to that of cyanic into cyanuric acid, in which, as is well known, a molecule of the one splits up into three of the other." This conception harmonises with that of Erlenmeyer,[3] who in 1870 made the following communication on the possible formation of polymeric modifications of carbonic acids: "I consider it possible, and indeed probable, that in the case of acids as well as of

aldehydes—the acids being in fact nothing but hydroxy-aldehydes —polymeric compounds occur, so that two or more molecules of different acids can unite to form a larger chemical molecule. This assumption would help to explain not only margaric acid, cinnamic acid (elaidic acid?), but also racemic acid, and perhaps maleic acid, as well as many peculiar relations observed in the conduct of certain other acids."

On account of the great analogy which the exhaustive researches of Kekulé [1] and of Fittig [2] have shown to exist between mesaconic and fumaric acids, on the one hand, and citraconic and maleic acids on the other, it would appear to be justifiable to apply to the analogous acid an hypothesis put forward to explain one of these acids. I mention this because Henry [3] in 1875 regarded mesaconic acid as being in all probability a polymeric modification of citraconic acid. One year later Markownikoff [4] was of the decided opinion that mesaconic acid is a polymeric modification of citraconic acid. This belief on the part of Markownikoff as well as of Henry was occasioned by a consideration of the melting points of the two acids, and of the fact that citraconic acid is changed to mesaconic acid by heating it with nitric, hydrochloric, or hydriodic acid. In harmony with this view of Markownikoff is the view of Erlenmeyer [5] recently communicated. Contrary to his former belief, he regards fumaric acid as a polymer of maleic acid, having a constitution similar to that of racemic acid. He says : " Racemic acid is certainly a double molecule, composed of dextro and lævo-tartaric acids ; fumaric acid is as certainly made up of two molecules of maleic acid :

Racemic acid.   Fumaric acid.
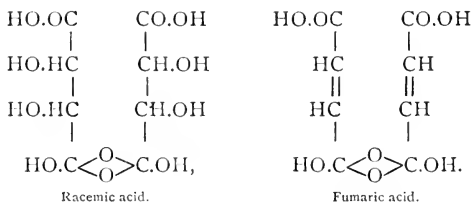
This conception has indeed much to commend it.   It was

[1] Annalen der Chemie, Sup. 1, 129, 358; 2, 85.   [2] Ibid. 188, 42; 195, 56, 169.
[3] Bull. Soc. Chim. 23, 353.   [4] Annalen der Chemie 182, 356.
[5] Berichte d. deutsch. chem. Gesell. 19, 1937.

shown some years ago by Kekulé and myself[1] that a generic relation exists between racemic and fumaric acids on the one hand and inactive tartaric and maleic acids on the other, since by oxidation with potassium permanganate, fumaric and maleic acids are converted into racemic and inactive tartaric acids respectively. At the close of our second paper we drew from these facts the following conclusion: "The nature of the isomerism of fumaric and maleic acids may perhaps be the same as that between racemic and inactive tartaric acids. Then, besides the inactive, there ought to exist two active modifications of maleic acid which should be obtained by the breaking up of fumaric acid." I will mention here that numerous attempts have been made to split up fumaric acid into its optically active components, according to methods employed in other cases, but without success.

Although it would not perhaps be difficult to assume from the result of the oxidation that fumaric acid is made up of dextro and lævo-maleic acids, still it would not necessarily follow; in fact, such an assumption would be unjustifiable if the theory of van t'Hoff-Le Bel is correct.[2] According to this theory, formulas for fumaric and maleic acids have been deduced, according to which the acids differ only in the relative positions in space of the carboxyls to the CH groups. Accepting this suggestion, an experimental solution of the question with regard to the isomerism of fumaric and maleic acids would scarcely be possible. As it is, it cannot but seem remarkable that so slight a difference in the position of the carboxyl groups should be the cause of such a fundamental difference in properties as is actually shown by fumaric and maleic acids.

To repeat—the generic relation of fumaric and racemic acids which Kekulé and myself have shown to exist, forms at present the only foundation for the supposition that fumaric acid has twice as large a molecule as maleic acid.

Erlenmeyer's formulas for fumaric and maleic acids show a possibility "of explaining apparently abnormal cases of isomerism and other cases of apparently abnormal behavior of organic acids,"

[1] Berichte d. deutsch. chem. Gesell. **13**, 2150; **14**, 713; cf. Tanatar, ibid. **12**, 2293; **13**, 159, 1383; Kekulé, Annalen der Chemie **117**, 124; Annalen der Chemie, Supp. **1**, 375; Perkin and Duppa, ibid. **117**, 130; Pasteur, Annalen der Chemie, Supp. **2**, 242; Jungfleisch, Bull. Soc. chimique **19**, 50, 194; **41**, 214, 226; Wyrouboff, ibid. **41**, 210; Pasteur, ibid. **41**, 215; Anschütz, Annalen der Chemie **226**, 191.

[2] Le Bel, Bull. Soc. chimique **22**, 337; **37**, 300; van t'Hoff, Lagerung der Atome im Raume bearbeitet von F. Hermann: Braunschweig, 1877, pp. 13, 21, 29.

but no experimental evidence of the correctness of this view has as yet been furnished. The van t'Hoff-Le Bel theory, which is opposed to the assumption of the existence of a dextro and lævo-maleic acid, assumes the simplest formula for fumaric acid, $\begin{array}{c} \text{CH.COOH} \\ \| \\ \text{CH.COOH,} \end{array}$

and ascribes the difference in properties of fumaric and maleic acids to different positions in space of the carboxyl groups.

I will now turn to the other hypotheses, according to which the fumaric and maleic acids have the same molecular weight, and the difference in the properties of the two acids is ascribed to a difference in the arrangement of the same number of atoms in the molecule. First, the chief argument in favor of the view that both acids have the same molecular weight will be considered as to its tenability.

It is often the custom, from the vapor density of a volatile derivative of a substance which is not itself volatile without decomposition, not only to draw conclusions concerning the molecular weight of the derivative, but also of the non-volatile substance itself in the solid state. Thus Hübner and Schreiber[1] have in this way shown that the vapor density of the ethyl ether of fumaric acid and that of maleic anhydride correspond to the simple formula of both substances. They have therefore concluded that the solid fumaric and maleic acids themselves must also possess an equal molecular weight corresponding to the simple formula $C_4H_4O_4$. It is evident that such a conclusion is wrong in principle, and, to demonstrate this, an ether of racemic acid appeared to me most suitable for showing the generic relation between racemic and fumaric acids. At my request a vapor density determination of the ethyl ether of racemic acid was made by my friend Bennert, according to Hofmann's method.[2] This determination was in accordance with the simple formula $C_5H_{14}O_6$. This result was not surprising, since the ethers of racemic and dextro-tartaric acids, with the same alcoholic radicals, possess the same boiling point under like conditions of pressure. I further prepared the methyl ether of lævo-tartaric acid, and proved that it united with equal parts by weight of the methyl ether of dextro-tartaric acid, forming the methyl ether of racemic acid. It must therefore be supposed that the ethers of

[1] Zeitschr. f. Chem. [N. F.] **7**, 712; cf. Hübner, Ber. d. deutsch. chem. Ges. **14**, 210.
[2] Anschütz, Ber. d. deutsch. chem. Ges. **18**, 1399.

racemic acid on being heated up to their boiling points, even under diminished pressure, are resolved into the ethers of dextro and lævo-tartaric acid, which, when their vapors are cooled, unite again to form the ethers of racemic acid. It is therefore certain, from the generic relation existing between racemic and fumaric acids, that the vapor density of the ether of fumaric acid leading to the simple formula $C_8H_{12}O_4$, is no satisfactory proof of the simple formula of this ether, nor of fumaric acid itself—that is, it is no argument against the assumption of a double molecule.[1]

It is generally conceded that the acid properties of fumaric and maleic acids are due to the presence of two carboxyl groups. The formulas which would first naturally suggest themselves are

$$\begin{matrix} \text{CH.COOH} \\ \| \\ \text{CH.COOH,} \end{matrix} \qquad \begin{matrix} \text{C}\!\!<^{\text{COOH}}_{\text{COOH}} \\ \| \\ \text{CH}_2, \end{matrix}$$

Fumaric acid.   Maleic acid.
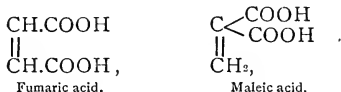
or *vice versa*. This conception, formerly held by V. v. Richter[2] and others, has been generally abandoned, since it does not harmonise with the general behavior and the simplest changes of both acids. I need only mention the formation of one and the same ethylene-succinic acid from both acids, and the fact that neither fumaric nor maleic acid loses carbon dioxide when heated.

All this has been discussed so often that it appears to me superfluous to go over it again. Kekulé[3] has proposed, in order to explain the formation of ethylene-succinic acid by the reduction of both acids, that in one of them, the maleic acid, a carbon atom be assumed to have two free bonds. If the presence of bivalent carbon atoms in organic compounds be regarded as possible, then it cannot be denied that, as Fittig[4] has shown some ten years ago, a large number of reactions with fumaric and maleic acids can be very easily and elegantly explained by the aid of the "incomplete formula for maleic acid." The following formulas for fumaric and

[1] I will mention that I caused a series of vapor density determinations to be made in this laboratory, of the different ethers of fumaric and maleic acids, and of mesaconic and citraconic acids. All the results pointed to a simple formula. They will be published in full as soon as a fitting opportunity presents itself.

[2] Zeitschr. f. Chem. [N. F.] **1**, 453.

[3] Annalen der Chemie, Supp. **2**, 111; Zeitschrift für Chemie **6**, 12; cf. Kolbe, Zeitschrift für Chemie **6**, 13; Erlenmeyer, ibid. **6**, 21; Claus, Theoretische Betrachtungen und deren Anwendungen zur Systematik der organischen Chemie, 200: Freiburg i. B., 1867.

[4] Annalen der Chemie **188**, 100; Berichte d. deutsch. chem. Gesell. **10**, 518.

maleic acids are still considered by Fittig[1] to be the best constitutional expressions for both acids:

$$
\begin{array}{ll}
\text{CH.COOH} & = \text{C.COOH} \\
\| & | \\
\text{CH.COOH,} & \text{CH}_2\text{.COOH.} \\
\text{Fumaric acid.} & \text{Maleic acid.}
\end{array}
$$
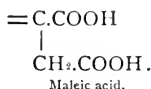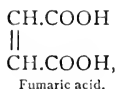
Beilstein[2] is of the same opinion, and so are most other chemists. If we ask ourselves why this formula be ascribed to maleic acid and not to fumaric, the answer may be found in the words of Rochleder,[3] who introduced the term "incomplete compound" into organic chemistry : " Maleic acid unites with bromine more readily than fumaric acid." Kekulé and Swarts,[4] at the close of their paper " On the Constitution of Itaconic, Citraconic, and Mesaconic Acids," express themselves as follows : " Fumaric acid is, for example, to be regarded as the analogue of mesaconic acid, and hence as the true homologue of mesaconic acid ; in maleic acid, however, free bonds are assumed, and it is known in fact that maleic acid forms addition-compounds more readily than its isomer fumaric acid."

Without considering that the slow addition of bromine by fumaric acid is caused by its difficult solubility and that of its addition-product, the ethers of fumaric acid unite with bromine as readily as any compound of maleic acid.[5] Consequently, the strongest reason for giving preference to this formula, $\begin{array}{c}=\text{C.COOH} \\ | \\ \text{CH}_2\text{COOH}\end{array}$

for maleic acid does not exist, and I believe that my assertion made some years ago that, with the same right, the formula $\begin{array}{c}=\text{C.COOH} \\ | \\ \text{CH}_2\text{.COOH}\end{array}$ could be given to fumaric acid, and the formula $\begin{array}{c}\text{CH.COOH} \\ \| \\ \text{CH.COOH}\end{array}$ to maleic acid, was perfectly justifiable.

One of the principal objections to the free bond formula, whether it be given to fumaric or to maleic acid, is the formation of racemic acid and inactive tartaric acid from fumaric and from maleic acids.

[1] Lehrbuch der organischen Chemie, 1887.   [2] Handbuch der organischen Chemie, 1886, 1, 616.
[3] Zeitschrift für Chemie 7, 261.   [4] Zeitschrift für Chemie [N. F.] 3, 651.
[5] Anschütz, Berichte d. deutsch. chem. Gesell. 12, 2282 ; 10, 1887.

These facts indicate that the group $\begin{matrix} \text{CH} \\ \| \\ \text{CH} \end{matrix}$ is present in both acids. The breaking up of the acids by electrolysis,[1] as well as the result obtained from the determination of the molecular refraction of their ethers,[2] lead to the same conclusion. If, however, the presence of the group $\begin{matrix} \text{CH} \\ \| \\ \text{CH} \end{matrix}$ be assumed in both acids, and it be assumed also that they have the same molecular weight, then the difference in their properties, if one does not seek refuge in van t'Hoff-Le Bel's hypothesis, must lie in the way the oxygen atoms and hydroxyl groups are united. In that case, of course, the view that in the molecule of each acid two carboxyls are contained must be abandoned. This leads to the three following conceivable formulas:

$$\text{I.}\ \begin{matrix}\text{CH.COOH}\\ \|\\ \text{CH.COOH}\end{matrix}; \qquad \text{II.}\ \begin{matrix}\text{CH—OH}\\ \|\quad\ \diagdown\text{O}\\ \text{CHC}=\text{O}\end{matrix}; \qquad \text{III.}\ \begin{matrix}\text{CH.C—OH}\\ \|\quad\wedge\\ \text{O O}\\ \|\quad\vee\\ \text{CH.C—OH}\end{matrix}.$$
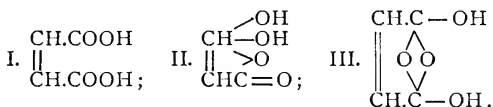
This possibility of escape from the dilemma with which organic chemistry is confronted by the isomerism of fumaric and maleic acids has hitherto received no attention, but it has already been mentioned twice, as far as I know, though only as a conjecture and without any effort to test it. As I shall now endeavor to *prove* that formula I. must be given fumaric acid, and that probably formula II. must be given to maleic acid, I will first quote certain statements of W. H. Perkin and W. Roser touching similar matters.

W. H. Perkin, Sen.,[3] found, among other things, that fumaric acid, on treatment with acetyl chloride, gives the same anhydride as maleic acid, and concerning this reaction he made the following observation:

"All these arguments apparently show the remarkable fact that only one anhydride is obtainable from fumaric and maleic acids, one only from citraconic and mesaconic acids, and, finally, only one from α and β-cumaric acids.

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[1] Kekulé, Annalen der Chemie **131**, 87.

[2] Gladstone, Berichte d. deutsch. chem. Gesell. **14**, 2544; Brühl, ibid. **14**, 2736; Kannonikoff, Journal f. prak. Chemie [N. F.] **32**, 500. At my request C. Knops has determined the molecular refractions of 12 ethers of maleic, fumaric, citraconic, mesaconic, and itaconic acids. The results will soon be published.—ANSCHÜTZ.

[3] Berichte d. deutsch. chem. Gesell. **14**, 2546.

" Upon what, then, can the isomerism of these acids depend, if not on the difference in position of the hydroxyl groups to the radicals?"

W. Roser expresses himself on this point much more decidedly :[1]

" The isomerism of the two diphenyldicarbonic acids, of the diphenylsuccinic acids, obtained by Reimer[2] from stilbene-dicarbonic acid, and which are converted into one another by treating either with hydrochloric acid or with barium hydrate, as the case may be, find a simple explanation in the following formulas:

$$\text{I.} \quad \begin{array}{c} \diagup \text{OH} \\ C_6H_5CH.C{-}OH \\ | \quad \diagdown O \\ C_6H_5CH.CO, \end{array} \qquad \text{and II.} \qquad \begin{array}{c} C_6H_5CH.COOH \\ | \\ C_6H_5CH.COOH. \end{array}$$
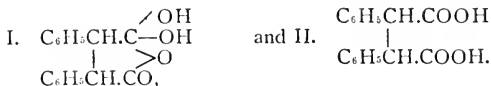
" The corresponding relations of maleic and fumaric acids and of the cumaric acids can perhaps be most easily explained by means of similar formulas." Roser adds:

" If the ethers of phthalic acid be constituted analogously to the first formula—that is, $C_6H_4 \left\{ \begin{array}{l} C{=}(OC_2H_5)_2 \\ \diagup O \\ CO, \end{array} \right.$ then their formation from phthalyl chloride is easily understood. On the other hand, there is indicated the possible existence of another isomeric phthalic acid and of another succinic acid."

It will be seen from the above how decidedly Roser's views have been influenced by the knowledge that the chloride of phthalic acid is unsymmetrically constituted. I will therefore call attention to the principal grounds for our present view regarding the constitution of this chloride.

As is well known, Hessert[3] first proved that by the reduction of phthalyl chloride there is formed, not the dialdehyde of *o*-phthalic acid, as was formerly supposed, but the inner anhydride of the *o*-alcohol-carbonic acid, $C_6H_4 \left\{ \begin{array}{l} CH_2OH\ (1) \\ COOH\ (2) \end{array} \right.$, to which he gave the name phthalide and the structural formula $C_6H_4 {<} \begin{array}{c} CH_2 \\ CO \end{array} {>} O$.

The counter-conclusion that phthalyl chloride is dichlorphthalide suggests itself, and is confirmed by the experiments of v. Baeyer,[4] who showed that phthalo-phenone, which is formed by treating

[1] Berichte d. deutsch. chem. Ges. **15**, 2347.   [2] Ibid. **14**, 1802.
[3] Ibid. **10**, 1445; **11**, 237.   [4] Annalen der Chemie **202**, 50.

phthalyl chloride and benzene with aluminic chloride, is a triphe-nylmethane derivative, viz. diphenylphthalide, $C_6H_4<\begin{matrix}C(C_6H_5)_2\\>O\\CO\end{matrix}$.

Proceeding on the supposition that phthalic acid contains two carboxyls and that therefore its silver salt should give symmetrical ethers, Graebe[1] attempted to obtain the unsymmetrical ethers from phthalyl chloride. In the case of phthalic acid itself he did not with certainty reach the expected result. With tetrachlorphthalic acid, however, he succeeded in preparing from the silver salt and ethyl iodide an ethyl ether melting at 60°, while from the chloride of tetrachlorphthalic acid and sodium alcoholate, the isomeric ethyl ether, melting at 124°, was obtained. Hence Graebe con-cludes : "There is here no other explanation possible than that the first compound has the formula $C_6H_4\begin{Bmatrix}CO_2C_2H_5\\CO_2C_2H_5\end{Bmatrix}$; while the second has this formula, $C_6H_4\begin{Bmatrix}C(OC_2H_5)_2\\>O\\CO.\end{Bmatrix}$"

As the experimental proof for the existence of two tetrachlor-phthalic acids was at that time wanting, Graebe did not consider the counter-conclusion based on the possibility of the existence of two isomeric tetrachlorphthalic acids. Again, the opinion that in a dicarbonic acid there must of necessity be two carboxyls was so deep-rooted that such formulas as $C_6Cl_4\begin{Bmatrix}C{<}{\begin{matrix}OH\\OH\end{matrix}}\\>O\\CO\end{Bmatrix}$ would not easily have been accepted without the most convincing proofs. Further, no difficulties were encountered in explaining the change of the chloride, $C_6H_4\begin{Bmatrix}CCl_2\\>O\\CO\end{Bmatrix}$, into the acid, as well as the reverse change.

The conception that many ketone-carbonic acids are oxy-lactones has recently been given an experimental basis by the important discovery of acetyl-lævulinic acid by Bredt.[2] Since the researches of Bredt, I no longer doubt that acetyl-lævulinic acid is to be regarded as γ-oxy-valero-lactone. I write the old and new formulas for the acid side by side:

$$\text{I.} \quad \begin{array}{l} \text{CH}_2.\text{CO.CH}_3 \\ | \\ \text{CH}_2\text{COOH;} \end{array} \qquad \text{II.} \quad \begin{array}{l} \qquad \diagup \text{CH}_3 \\ \text{CH}_2.\text{C}-\text{OH} \\ \quad | \qquad \diagdown \text{O} \\ \text{CH}_2.\text{CO.} \end{array}$$
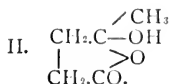
Bredt showed further that acetyl-lævulinic acid does not stand alone, but that in all probability a large number of γ-ketone acids have an analogous constitution. This essentially widens our conceptions regarding the nature of ketone acids. It is evident that according to this theory two series of isomeric compounds can be predicted, the γ-ketone acids and the γ-oxy-lactones. Doubtless the atoms or atomic groups which are in combination with the α-, β- and γ-carbon atoms have the greatest influence on the lactone formation; and further investigation is necessary to determine the conditions under which the γ-ketone acid or the corresponding γ-oxy-lactone is the most stable, and under what conditions both compounds can exist.[1] If these views concerning the γ-ketone acids be extended to the γ-dicarbonic acids, as Bredt has done at the close of his paper, then the isomeric γ-dioxylactones would stand in the same relation to the γ-dicarbonic acids as the γ-oxylactones to the γ-ketone acids. In the formulas of the γ-dioxylactones, two hydroxyls are, to be sure, united to the same carbon atom, but this is also the case in chloral hydrate, mesoxalic acid, the dioxy-tartaric acids and other compounds, in all of which this carbon atom, as in the new formula for maleic acid, is united to strongly negative groups.

Assuming now that in the unsaturated lævulinic acid, which is probably L. Wolff's co-called acetacrylic acid, and which bears the same relation to lævulinic acid that ethylene bears to ethane, viz.
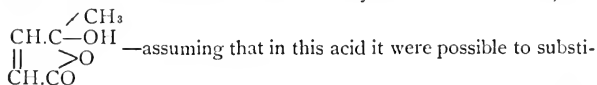
$$\begin{array}{l} \qquad \diagup \text{CH}_3 \\ \text{CH}.\text{C}-\text{OH} \\ \| \quad \diagdown \text{O} \\ \text{CH}.\text{CO} \end{array}$$ —assuming that in this acid it were possible to substitute hydroxyl for methyl, an acid of the formula

$$\begin{array}{l} \qquad \diagup \text{OH} \\ \text{CH}.\text{C}-\text{OH} \\ \| \quad \diagdown \text{O} \\ \text{CH}.\text{CO} \end{array}$$

would be obtained. This would be maleic acid, if the new formula for this acid is correct.

[1] On comparing lævulinic and succinic acids, one is led to think that perhaps the two isomeric modifications of the unsaturated lævulinic acid corresponding to fumaric and maleic acids could be more easily obtained than those of lævulinic acid itself. Dr. Bredt has informed me that he has for a long time been occupied with researches in this direction.—ANSCHÜTZ.

It would, on the other hand, be a very strong argument in favor of the new formula of maleic acid if we could prepare maleic acid from the unsaturated lævulinic acid, according to the method mentioned above. According to my views this was effected several years ago.

Kekulé and Strecker[1] showed that trichlorphenomalic acid is unsaturated lævulinic acid in which the hydrogen atoms of the methyl are replaced by three chlorine atoms. Trichlorphenomalic acid has, according to its description, all the peculiarities of a lactone in a higher degree than lævulinic acid. It has a pleasant odor and is volatile with water vapor. We therefore propose in place of the formula of Kekulé and Strecker for the trichlorphenomalic acid, one in which the acid appears to be the isomeric γ-oxylactone of β-trichloracetacrylic acid :

$$
\text{Trichlorphenomalic acid:} \quad
\begin{array}{c}
\text{CHCO.CCl}_3 \\
\parallel \\
\text{CH.COOH,} \\
\text{\scriptsize Old formula.}
\end{array}
\qquad
\begin{array}{c}
\qquad\diagup\text{CCl}_3 \\
\text{CH.C} - \text{OH} \\
\parallel \qquad \diagup\text{O} \\
\text{CH.C} = \text{O.} \\
\text{\scriptsize New formula.}
\end{array}
$$
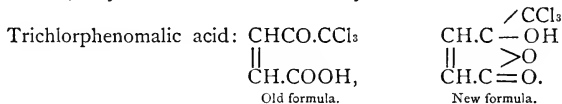
On treating trichlorphenomalic acid with a solution of barium hydrate, there is formed, as Kekulé and Strecker[2] have shown, chloroform and the barium salt of maleic acid, and, according to my views, this reaction takes place in the sense of this equation :

$$
\begin{array}{c}
\qquad\diagup\text{CCl}_3 \\
\text{CH.C}-\text{OH} \\
\parallel \qquad\diagup\text{O} \\
\text{CHC} = \text{O}
\end{array}
+ \text{Ba(OH)}_2 =
\begin{array}{c}
\text{CH.C}\diagup\text{O}\diagdown\text{Ba} \\
\qquad\diagdown\text{O}\diagup \\
\parallel \qquad\diagup\text{O} \\
\text{CH.C} = \text{O}
\end{array}
+ \text{CCl}_3\text{H} + \text{H}_2\text{O.}
$$
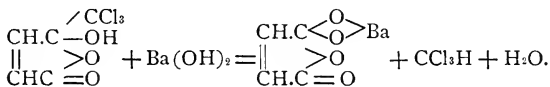
This and other reactions of trichlorphenomalic acid are in harmony with the formula proposed by me for this acid.

In complete harmony with this conception of the change undergone by trichlorphenomalic acid when treated with alkalies or alkaline earths are the results of the valuable researches of Hill and Sanger,[3] "On the brompyromucic acids." The principal products of the transformations of these acids are, throughout, derivatives of maleic and not of fumaric acid. In all the brompyromucic acids, the "ethylene oxide oxygen," which is required for the γ-dioxylactone formula of maleic acid, is already present.

It would lead too far should I, starting with this new formula for maleic acid, attempt an interpretation of the numerous investi-

gations made by Hill and Sanger.[1] I will therefore content myself by calling attention to one point.

It was formerly believed that mucochloric and mucobromic acids were the substitution-products of the half aldehydes of fumaric acid, and lately, of maleic acid. It appears to me that there can be but little doubt that these substances should be represented by formulas which are analogous to those of lævulinic and maleic acids, thus:

$$
\begin{array}{ccc}
\underset{\text{Mucobromic acid.}}{\begin{array}{c} \text{CBrC} \overset{\text{H}}{\diagup} \text{OH} \\ \| \diagdown \!\! \text{O} \\ \text{CBrC} = \text{O} , \end{array}}
&
\underset{\text{Mucochloric acid.}}{\begin{array}{c} \text{CClC} \overset{\text{H}}{\diagup} \text{OH} \\ \| \diagdown \!\! \text{O} \\ \text{CClC} = \text{O} , \end{array}}
&
\underset{\text{Acetyl mucochloric acid.}}{\begin{array}{c} \text{CCl.C} \overset{\text{H}}{\diagup} \text{O.COCH}_3 \\ \| \diagdown \!\! \text{O} \\ \text{CCl.C} = \text{O}. \end{array}}
\end{array}
$$
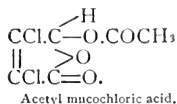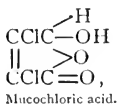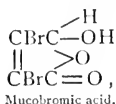
The acetyl compound of mucochloric acid prepared by Jackson and Hill,[2] and which is evidently analogous to acetyl-lævulinic acid, speaks in favor of the correctness of the above formulas, according to which it is seen that the substances mentioned do not behave like aldehydes.

Maleic acid is therefore to be regarded as a lactone derivative of γ-oxycrotonic acid, and as the dioxylactone of this acid. If we suppose both halogens in the mucochloric or mucobromic acids to be replaced by two hydrogen atoms, the result is the monoxy-lactone of γ-oxycrotonic acid, which is perhaps the so-called "half aldehyde" of fumaric acid.[3] The relation of these substances is illustrated in the following formulas:

$$
\left(\begin{array}{c} \text{CH.CH}_2 \\ \| \diagdown \!\! \text{O} \\ \text{CH.CO} \end{array} \right) , \qquad
\begin{array}{c} \text{CHCH(OH)} \\ \| \diagdown \!\! \text{O} \\ \text{CHCO} \end{array} , \qquad
\begin{array}{c} \text{CHC(OH)}_2 \\ \| \diagdown \!\! \text{O} \\ \text{CHCO} . \end{array}
$$
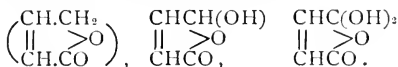
If maleic acid be indeed a γ-dioxylactone, it ought to be possible to break the lactone ring. Then, if it be further possible to retain the carboxyl formed as a result of this separation, and to add a carboxyl to the γ-carbon atom, the acid thus formed would be fumaric acid. If such a reaction is to prove anything with regard to the constitution of fumaric acid, those reagents must of course be avoided which would convert free maleic into fumaric acid. In the foregoing paper, by Mr. Wirtz and myself, the experimental solution of this problem is described, and I will now discuss the results of the investigation.

[1] Annalen der Chemie **232**, 42.   [2] This Journal **3**, 46.
[3] Limpricht, Annalen der Chemie **165**, 285.

On heating maleic anhydride with aniline there is formed, together with the anil of phenyl-aspartic acid, the anil of maleic acid, which must have one of the two following formulas :

$$\text{I. } \begin{array}{l} \text{CH.CNC}_6\text{H}_5 \\ \| \quad >\text{O} \\ \text{CH.CO} \end{array} ; \qquad \text{II. } \begin{array}{l} \text{CHCO} \\ \| \quad >\text{NC}_6\text{H}_5 \\ \text{CHCO} \end{array} .$$
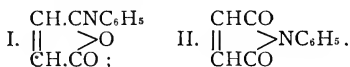
In either way the maleinanil may be regarded as a derivative of maleic anhydride. On treating maleinanil with ammonia, or better with barium hydrate solution, salts of the anilic acid are formed, which, whether formula I or II be correct, has the following constitution :

$$\begin{array}{l} \text{CH.CONHC}_6\text{H}_5 \\ \| \\ \text{CH.COOH} \end{array} .$$
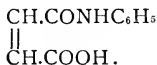
The ring of maleic acid is broken, a carboxyl is formed, and it only remains to replace the aniline residue by hydroxyl. This is easily accomplished through saponification with an alcoholic solution of potassium hydrate. The product is fumaric acid. The anilic acid obtained from maleinanil must be regarded as a derivative of fumaric acid, and as fumaranil; for, to the best of our knowledge, all conditions tending to change maleic acid, if it were first formed, into fumaric acid have been avoided. Fumaric acid, therefore, in all probability contains two carboxyl groups, which view is strengthened by Claissen and Thomson's[1] synthesis of fumaric acid.

The researches of Ostwald,[2] on the electrical conductivity of fumaric and maleic, and of mesaconic and citraconic acids, are in accord with these results. To be sure, Ostwald sees in his investigations arguments in favor of the formulas of Kekulé, Swarts and Fittig for maleic and citraconic acids; but Ostwald calls attention to the similarity in the behavior of maleic acid to that of phosphorous and selenous acids, which, as he will probably freely admit, is more striking on the assumption of the dioxylactone formula for maleic acid than on the assumption of any one of the other expressions heretofore proposed. Now, as the constitution of maleic acid from a study of its chemical changes appears to a certain degree established, the investigations of the electrical

[1] Annalen der Chemie **218**, 169.   [2] Journ. prakt. Chem. [N. F.] **32**, 362.

conductivity might become a very valuable aid in the determination of the constitution of dicarbonic acids.

As a conclusion to my arguments, having for their object the establishment of the dioxylactone formula for maleic acid, and the dicarboxyl formula for fumaric acid, I should like to point out some of the most important inferences that may be drawn therefrom.

Since fumaric and maleic acids are for the most part converted by oxidation into racemic and inactive tartaric acids respectively, it is very probable that racemic acid is to be regarded as a carboxyl acid, and inactive tartaric acid as a dioxylactone. Owing to the great analogy of fumaric to mesaconic acid and of maleic to citraconic acid, the corresponding acids must be analogously constituted, thus:

$$\begin{array}{ccc}
\text{CH}_3\text{C.COOH} & \text{CH}_3\text{C.C(OH)}_2 & \text{CH.C(OH)}_2 \\
\| & \| \quad >\!\!\text{O} \quad \text{or} & \| \quad >\!\!\text{O} \\
\text{CH.COOH,} & \text{CHCO,} \quad \text{CH}_3\text{C.} & \text{CO.} \\
\text{Mesaconic acid.} & \multicolumn{2}{c}{\text{Citraconic acid.}}
\end{array}$$
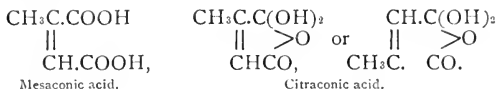
Citraconic acid could accordingly be regarded as the dioxylactone of γ-oxy-a or γ-oxy-β-methyl-crotonic acid. The theory allows two isomeric modifications of citraconic acid, and I must leave it to time to decide which of these modifications represents the known citraconic acid. The mono-substitution products and the halogen addition-products of fumaric and maleic acids may be represented by analogous formulas:

$$\begin{array}{ccc}
\text{CH.COOH} & \text{CBr.C(OH)}_2 & \text{CH.C(OH)}_2 \\
\| & \| \quad >\!\!\text{O} \quad \text{or} & \| \quad >\!\!\text{O} \\
\text{CBr.COOH,} & \text{CH.CO,} & \text{CBr.CO,} \\
\text{Monobromfumaric acid.} & \multicolumn{2}{c}{\text{Monobrommaleic acid.}}
\end{array}$$

$$\begin{array}{cc}
\text{CHBr.COOH} & \text{CHBr.C(OH)}_2 \\
| & | \quad >\!\!\text{O} \\
\text{CHBr.COOH,} & \text{CHBr.CO.} \\
\text{Ordinary dibromsuccinic acid.} & \text{Isodibromsuccinic acid.}
\end{array}$$
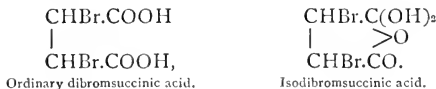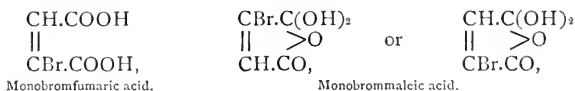
The tendency of unsaturated acids to form anhydrides increases with the replacement of the hydrogen, in union with doubly linked carbon atoms, by alkyl residues or halogen atoms. This is shown in the behavior of dibrommaleic and bromcitraconic acids.

It can now be easily understood why maleic and fumaric acids, monobrommaleic and monobromfumaric acids, citraconic and

mesaconic acids, are capable of forming only one anhydride; and why maleic and citraconic acids are so much more readily converted into anhydrides than fumaric or mesaconic acids. On the other hand, the difference in the salts, ethers and chlorides of the acids is just as easily explained.

We find, for the first time, in this dioxylactone formula for maleic acid a satisfactory explanation of the change of maleic into fumaric acid by mineral acids. Further research is necessary, however, before a satisfactory interpretation of the change of maleic acid ethers into those of fumaric acid can be given.[1] At first glance there appears to be a contradiction here, inasmuch as the treatment of the lactone-maleic acid with hydrochloric acid gives fumaric acid, while in other cases a solution of hydrochloric acid promotes the formation of lactones from oxyacids. The contradiction is, however, only apparent. The lactone ring of maleic acid, as in the case of other lactones, is capable of being broken by hydrochloric acid; the chlorine in the case of maleic acid unites with the carbon atom, with which the two hydroxyls are connected. This chlorine atom can unite to form hydrochloric acid either with the hydrogen of the neighboring hydroxyl or with the hydrogen of the carboxyl in the γ-position. The first takes place, and fumaric acid is formed according to the following equation:

$$\begin{array}{ll} \text{CH.C(OH)}_2 & \text{CH.COOH} \\ \| \quad \diagdown \text{Cl} \; - \; \text{HCl} = \; \| \\ \text{CH.COOH} & \text{CH.COOH.} \end{array}$$
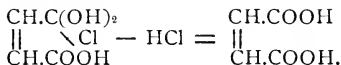
The formation of the same monobromsuccinic acid by the action of hydrobromic acid on fumaric and maleic acids is a necessary consequence of the general behavior of the halogen acids towards maleic acid.

The results of the chemical and physical investigations on fumaric and maleic acids and on their ethers accord better with the formulas proposed by me for these substances than with any of the earlier hypotheses. And it is certainly advisable to give more consideration to the physical properties than has hitherto been the custom in speculations on the constitution of organic compounds.

[1] Ber. d. deutsch. chem. Ges. **11**, 1644; **12**, 2280.—I have carried my observations further and found that the change appears to have certain limits — that is, that nearly but not quite all the maleic acid ether which is used in the reaction is changed into the corresponding fumaric acid ether. A separation of the ethers themselves involves insurmountable difficulties, and it is only because I have succeeded in finding a method of separation, depending upon the properties of the barium salts, that I hope to be able to carry the investigations to an end.—ANSCHÜTZ.

I wish especially to emphasise the fact that by the assumption of the dioxylactone formula for maleic acid, the van t'Hoff-Le Bel's formula for this acid would have to be given up. The explanation given by van t'Hoff-Le Bel concerning the relations of fumaric and racemic acids would, on the other hand, not be affected in the least by the new formula for maleic acid.

The isomerism of fumaric and maleic acids descends, to be sure, from the region of geometrical isomerism to that of ordinary isomerism. Under these circumstances it is not necessary for me to discuss the conception of alloisomerism introduced by Michael.

In the above transformations of fumaric and maleic acids I have not mentioned the formation of one succinic acid from both maleic and fumaric acids, not because I considered it difficult to give a plausible explanation of these facts on the basis of the formulas for fumaric and maleic acids defended by me, but because it seemed to me doubtful whether we have, in ordinary succinic acid, a dicarboxyl acid or a dioxylactone ; and, further, the possible modification, still undiscovered, may in time be found. Besides, in the face of the evident influence which the atoms and atomic groups in union with the α- and β-carbon atoms exert on the behavior of both hydroxyl groups, I am far from assuming that the isomers corresponding to fumaric and maleic acids of every γ-dicarbonic acid can be isolated.

These considerations show that, among the methods of formation and transformation of fumaric and maleic acids, not one is inconsistent with the assumption of the dioxylactone formula for maleic acid. I even venture to assert that in the light of the earlier views concerning the isomerism of fumaric and maleic acids, the reactions described by me—viz. the formation of maleic acid from trichlorphenomalic acid ; the formation of bromine derivatives of maleic acid from the bromine derivatives of the furfuran group ; the formation of fumaric acid from maleinanil—cannot be understood at all, or only by the aid of less probable assumptions.

It would be a simple matter to apply to a greater extent than has been done in this paper, the consequences resulting from a consideration of the dioxylactone formula, to those isomeric dicarbonic acids which show differences of behavior similar to those of fumaric and maleic acids. I have, however, omitted such a generalisation, believing it better to wait till other investigations

have proved that the isomerism of any two dicarbonic acids is of a nature similar to that of fumaric and maleic acids. Investigations of this kind have for some time been in progress in this laboratory on the isomeric camphoric, dimethylsuccinic, diphenylsuccinic acids, etc. Above all, researches undertaken by Mr. Bendix and myself on the diphenylsuccinic acids, as well as on diphenylmaleic anhydride, seem to me to be of especial interest. If indeed the isomerism of both diphenyl-succinic acids is of the same nature as that of fumaric and maleic acids, then it would be *proved* that the difference between these latter acids cannot possibly be ascribed to the existence in one of these acids of a carbon atom with two free bonds, as this is impossible in the case of diphenylsuccinic acids.

Bonn, *March* 20, 1887.

ON A COMPOUND OF MANGANESE SESQUIOXIDE WITH CUPRIC OXIDE.

By E. A. Schneider.

The compounds of the sesquioxides of aluminium, chromium, and iron with basic oxides have already been prepared by many different methods. I have searched the chemical literature in vain for a description of compounds in which either manganese sesquioxide acts as an acid toward the oxides with strongly basic properties, or the oxides of copper, silver, and mercury as bases towards the sesquioxides in general.[1] This fact, in connection with the well-known properties of these oxides, properties which indicate an analogy on the one hand between manganese sesquioxide and the sesquioxides of iron, chromium, and aluminium, and on the other hand between the oxides of copper, silver, and mercury and those of the alkali metals, led me to think that compounds of the kind referred to might be made.

Many compounds of metallic oxides are known, among which may be mentioned the aluminates and analogous compounds of iron and chromium. As is well known, the principal representatives of the group of aluminates, the spinels, are to be regarded

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[1] I have found two compounds mentioned belonging to the latter class. $CuOFe_2O_3.5HO$ is mentioned in Frémy's Encyclopédie chimique, but without naming the original article; $CuO.Cr_2O_3$ is described by Gerber, Bull. de la Soc. chim. **27**, 435.

as salts of the acid AlO.OH. Thus spinel itself is $(AlO.O)_2Mg$ or $\dfrac{AlO.O}{AlO.O} {>} Mg$; similarly, cymophane is $(AlO.O)_2Be$; hercinite is $(AlO.O)_2Fe$. These have been made artificially by Ebelmen.[1] Chromite is an analogous compound and is represented by the formula $(CrO.O)_2Fe$.

Gerber[2] obtained compounds of chromic oxide with the oxides of calcium, barium, magnesium, iron, zinc, and copper. The reaction which he used consisted in heating to red heat a mixture of potassium bichromate with an anhydrous metallic chloride: $MCl_2 + K_2Cr_2O_7 = 2KCl + (CrO.O)_2M + 3O$. In this equation M represents a bivalent metal.

Zincates and cuprates of the strong bases have also long been known. Thus Berzelius described a zincate, $ZnO.K_2O = Zn(OK)_2$; and Frémy[3] one of the composition $2ZnO.K_2O = \dfrac{Zn}{Zn}{<}\genfrac{}{}{0pt}{}{OK}{O}_{OK.}$

Loew[4] described a very unstable compound, $CuO.Na_2O = Cu(ONa)_2$.

Taking into account the statement of Berzelius that the existence of zincates of the alkaline earth metals is probable, and the negative results which I obtained in trying to prepare analogous compounds of copper, I concluded that the acid properties of zinc oxide are far stronger than those of cupric oxide. Considering on the other hand the more basic than acid properties of cupric oxide; further, the fact that chromic oxide and ferric oxide combine with cupric oxide, and that, in the natural arrangement of the elements according to Mendelejeff, manganese occupies the place between chromium and iron, I concluded that manganese sesquioxide would also in all probability combine with cupric oxide. The experiment has confirmed this supposition.

None of the previously mentioned reactions seemed to me to be adapted to my purpose. The application of high temperatures was entirely excluded, as cupric oxide and manganese sesquioxide are changed at a high heat. The reaction of Pelouze (precipitation of a mixture of manganous chloride and copper chloride in certain molecular proportions by an excess of potash) did not promise to be of much use. More promising appeared to me a

[1] Ann. Chim. Phys. [3] 22, 213; 33, 34.   [2] Bull. Soc. chimique 27, 435.
[3] Comptes rendus 15, 1106.   [4] Zeitschrift f. an. Chemie 9, 463.

reaction which Berzelius[1] mentions in a paper on zinc oxide. He states that Sander had obtained a zincate of alumina or an aluminate of zinc by mixing a solution of alumina in caustic potash with zinc oxide ammonia.

Now I had noticed, when experimenting with the blue solution which results from the treatment of copper with ammonia in presence of air, and which is commonly though wrongly called copper oxide ammonia, how very slowly cupric hydrate is precipitated from it by caustic alkalies, even in very dilute solutions.

To 50 cc. of such a solution containing 0.4906 gram CuO I added 100 cc. caustic soda (sp. gr. = 1.4) and 500 cc. water. After standing ten days at ordinary temperature a considerable precipitate had formed, but the solution still remained blue.

This behavior of copper salts towards caustic alkalies in ammoniacal solution seemed to me very favorable for the purpose of testing the affinity of manganese sesquioxide towards cupric oxide.

Manganous hydroxide is instantly thrown down from solutions of manganous salts by caustic alkalies. By the access of air the manganous compound is changed to the manganic compound. If now this reaction is carried out in presence of a copper salt in ammoniacal solution, and if a strong affinity exists between copper oxide and manganic oxide, the former must also be instantly precipitated and combine with the manganic oxide.

I used the following solutions in my experiments:

1. The blue solution which is obtained by repeatedly pouring ammonia over copper scraps in presence of air. According to Peligot,[2] this solution is not copper oxide ammonia, as commonly supposed, but it contains a salt of the composition $Cu(NO_2)_2$ $2NH_3 + 2H_2O$, a double compound of nitrite of copper and ammonia. Submitted to a temperature of 100° this salt loses ammonia and water until copper nitrite, $(NO_2)_2Cu$, remains behind.

The solution which I have employed contained 13.8960 grams CuO per liter.

2. A solution of manganous chloride containing 36.33 grams Mn_2O_3 per liter.

3. Caustic potash (sp. gr. = 1.2).

[1] Ann. der Chemie **9**, 181.　　　　[2] Ann. Chim. Phys. [3] **63**, 343.

First Series of Experiments.

Four portions of the ammoniacal copper salt solution represent-
ing respectively 1, 2, 3 and 4 molecules of CuO were mixed each
with 100 cc. of the caustic potash. To each portion a quantity of
the solution of manganous chloride, representing in each case one
molecule of Mn_2O_3, was added at once. After the lapse of one
hour, during which the mixtures were frequently stirred, they were
diluted with water to about 500 cc., frequently decanted, and the
precipitate brought on a filter and washed with hot water until the
wash water no longer showed an alkaline reaction.

1. In the case in which the solution contained 1 mol. Mn_2O_3 to 1
mol. CuO the results were as follows :

After addition of the manganous chloride the deep blue solution
instantly became colorless and a black precipitate settled to the
bottom.

2. With the proportion 1 mol. Mn_2O_3 to 2 mol. CuO the results
were the same as in 1.

3. With the proportion 1 mol. Mn_2O_3 to 3 mol. CuO the super-
natant liquid appeared, after the same lapse of time which solutions
1 and 2 had been allowed to stand, deep blue.

The precipitate formed in this case was dried to a constant
weight at 100° C., and afterwards heated over a Bunsen burner
until no further loss in weight took place. It was then dissolved
in hydrochloric acid, the copper precipitated with hydrogen
sulphide, and the manganese determined in the filtrate by precipi-
tating as carbonate and weighing as the oxide Mn_3O_4. The
manganese found in this way, calculated on the basis of the precipi-
tate dried at 100°, corresponded to 50.38 per cent. Mn_2O_3, and
calculated on the basis of the precipitate heated to a high temper-
ature it corresponded to 50.71 per cent. Mn_3O_4.

4. With the proportion 1 mol. Mn_2O_3 to 4 mol. CuO the super-
natant liquid remained deep blue. The precipitate dried at 100°
contained an amount of manganese corresponding to 43.47 per
cent. Mn_2O_3, and when heated to a high temperature the manga-
nese corresponded to 44.18 per cent. Mn_3O_4.

All the precipitates were black, and acquired a brownish tinge
after being dried at 100° C. They dissolved in chlorhydric acid,
with evolution of chlorine, even before being dried. As a compound
of the composition $Mn_2O_3.2CuO$ contains 49.87 per cent. Mn_2O_3

(Mn $=$ 55, Cu $=$ 63.4), the results of experiment No. 3 led me to believe that manganese sesquioxide combines with only two molecules of cupric oxide. The results of experiment No. 4 suggested a slight modification in order to ascertain the maximum of cupric oxide that can combine with manganese sesquioxide. Instead of adding the manganous chloride all at once, I allowed it to drop very slowly into the mixture of the ammoniacal copper salt and caustic potash, and kept the mixture constantly stirred. The precipitates obtained in this way contained a quantity of manganese corresponding very nearly to the formula $Mn_2O_3.3CuO$.

Second Series of Experiments.

1. When the solution contained 1 mol. Mn_2O_3 to 3 mol. CuO the supernatant liquid was pale blue.

The precipitate, after being heated to a high temperature, contained a quantity of manganese corresponding to 44.21 per cent. Mn_3O_4.

2. Proportion 1 mol. Mn_2O_3 to 3 mol. CuO. The supernatant liquid was of a pale blue color. The precipitate dried at 100° contained 44.06 per cent. Mn_2O_3, and heated to a high temperature it contained 44.42 per cent. Mn_3O_4.

3. Proportion 1 mol. Mn_2O_3 to 4 mol. CuO. The supernatant liquid was deep blue. The precipitate dried at 100° contained 40.28 per cent. Mn_2O_3 and 54.54 per cent. CuO (total, 94.82 per cent.) ; heated to a high temperature it contained 40.96 per cent. Mn_3O_4 and 57.45 per cent. CuO (total, 98.45 per cent.).

4. Proportion 1 mol. Mn_2O_3 to 5 mol. CuO. The supernatant liquid was deep blue. The precipitate dried at 100° contained 40.02 per cent. Mn_2O_3 and 56.51 per cent. CuO (total, 96.53 per cent.); heated to a high temperature it contained 41.63 per cent. Mn_3O_4 and 59.08 per cent. CuO (total, 100.71 per cent.).

It will be seen from the above results that the composition of the precipitate approaches very nearly that of a compound $Mn_2O_3.3CuO$ which requires 39.88 per cent. Mn_2O_3 and 60.12 per cent. CuO. From experiments 3 and 4 it is further clear that an excess of at least 1 or 2 molecules of cupric oxide above that required by theory favors the formation of the compound $Mn_2O_3.3CuO$. The considerable deficit in the summation of the analyses, particularly of the precipitates dried at 100°, is to be

ascribed to water, which apparently requires a higher temperature for complete expulsion, and also to silica, as I had omitted to purify the caustic potash by alcohol.

I have made two more experiments with an ammoniacal solution of cupric chloride and the same solutions of manganous chloride and caustic potash.

This time I did not work with previously determined quantities of the reagents, but added the manganous chloride solution drop by drop to a concentrated ammoniacal solution of cupric chloride which was previously mixed with an excess of caustic potash. The addition of manganous chloride was stopped when the liquid was still deep blue, and the precipitate then filtered off and analysed in the usual way. The strongly ignited precipitates contained (1) 49.40 per cent. CuO, and (2) 53.43 per cent. CuO.

A larger number of experiments will no doubt throw light on the question which copper salt is best adapted to the reaction.

I have performed similar experiments qualitatively with ammoniacal solutions of silver oxide and of zinc oxide, and have found that silver oxide combines with manganese sesquioxide, but that zinc oxide does not.

It is a pleasant duty for me to thank Professor E. W. Hilgard for the kind permission to use the laboratory which is under his direction.

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RESEARCHES ON ALLOISOMERISM.

II.

BY A. MICHAEL AND G. M. BROWNE.

It is in the compounds of the butyl series that those instances of isomerism and peculiar properties of certain derivatives, that cannot be explained by the present theories of structural chemistry, are first shown in a marked degree. The properties of the a- and β-hydroxy-fatty acids stand in a close relation to their structural formulae ; but the instability of the γ-hydroxy-acids is a fact before which the present theories stand perfectly helpless in offering an

explanation. There is no doubt that the explanation will be found in the atomic grouping of the molecule in space; and, as the derivatives of the higher series of fatty compounds are those that particularly show these apparently anomalous properties, it is through their investigation that our knowledge of atomic grouping in space must be gained. A class of compounds that very noticeably show a relation to grouping in space are the crotonic acids and their halogen derivatives, and the correct interpretation of their constitution is certain to have considerable influence on the chemical theories of the structure of organic compounds.

The difficulty in classifying the crotonic acids begins in the formation of the solid acid from allyl cyanide. According to this synthesis it should have the constitution $CH_2 — CH — CH_2 — COOH$, and indeed it was universally assigned to it[1] until Kekulé[2] showed that its behavior towards fused alkalies would not admit of this constitution, but agreed with $CH_3 — CH — CH — COOH$. An explanation has been offered by Pinner,[3] but the subject can hardly be considered as on a satisfactory basis. A second crotonic acid was discovered by Geuther[4] in 1871. This chemist obtained two isomeric chlorcrotonic acids by the action of phosphorus pentachloride on acetacetic ether, and the reduction of β-chlorisocrotonic acid gave a liquid crotonic acid, while the β-chlorcrotonic acid gave the solid acid. The constitutions generally adopted for these acids are $CH_3 — CCl — CH — COOH$ for β-chlorcrotonic acid, $CH_2 — CCl — CH_2 — COOH$ for β-chlorisocrotonic acid, and $CH_2 — CH — CH_2 — COOH$ for isocrotonic acid, although the formation of a compound represented by the adopted constitution of β-chlorisocrotonic acid is contradictory to all our knowledge concerning the splitting off of a halhydric acid from an organic halogen acid. A third chlorcrotonic acid has been obtained by the reduction of trichlorbutyric acid, and undoubtedly has the constitution $CH_3 —· CH — CCl — COOH$.[5]

A different conception of the constitution of the acids obtained by Geuther is due to van't Hoff,[6] who considered both the chloro-

[1] Lwow, Berichte d. deutsch. chem. Gesell. **3**, 96; Paterno and Amato, Comptes rendus **69**, 479; Claus, Berichte d. deutsch. chem. Gesell. **3**, 181; Erlenmeyer, Lehrbuch, 312; Tollens, Zeitschrift für Chemie, 1871, 253; Rinne and Tollens, Annalen der Chemie **159**, 105.
[2] Berichte d. deutsch. chem. Gesell. **3**, 608; Annalen der Chemie **162**, 114.
[3] Berichte d. deutsch. chem. Gesell. **12**, 2053.
[4] Zeitschrift für Chemie, 1871, 242; Geuther and Frölich, ibid. 1869, 270.
[5] Krämer and Pinner, Annalen der Chemie **158**, 37; Sarnow, ibid. **164**, 93; Friedrich, ibid. **219**, 368.   [6] La Chimie dans l'espace.

acids formed in the action of phosphorus pentachloride on acetacetic ether as having the constitution $CH_3 — CCl — CH — COOH$, and isocrotonic acid as having the same constitution as solid crotonic acid. This view has been in some degree corroborated by the experiments of Friedrich,[1] who found that the chloro-acids gave the same ethoxy-acid when heated with sodium ethyl oxide; and by C. Kolbe,[2] who made the interesting observation that iso-crotonic acid on treatment with bromine gave the α,β-dibrombutyric acid that had been obtained in the same way from solid crotonic acid. On the other hand, Autenrieth[3] has very recently obtained isomeric phenylmercapto-crotonic acids by treating the chloro-acids with sodium phenyl sulphide; facts, however, that do not speak against the van't Hoff constitutional formulae. It is also worthy of note that Hemilian[4] found that isocrotonic acid can be converted by heating into solid crotonic acid, and Friedrich[5] that β-chlorcrotonic acid can be converted in the same way into β-chlorisocrotonic acid. The mono-bromo-derivatives of crotonic acids are represented by two acids. An alpha-acid has been obtained by decomposing α-dibrombutyric acid with alkalies, and an iso-meric acid by treating α,β-dibrombutyric acid in the same manner.[6] In order to explain this isomerism the second acid was given the constitution $CH_3 — CBr — CH — COOH$, which structural formula, though universally adopted, had no further proof than the fact that the isomerism of the two acids could be explained by the assumption.[7]

In the present paper we have endeavored to bring conclusive proofs that the generally accepted constitutions of β-chlorisocrotonic and so-called β-bromcrotonic acids cannot be longer upheld, and we also have been able to obtain a second α-chlorcrotonic and a β-bromcrotonic acid.

[1] Annalen der Chemie **219**, 322.   [2] Journal f. prak. Chemie [2] **25**, 396.
[3] Berichte d. deutsch. chem. Gesell. **20**, 1531.   [4] Annalen der Chemie **174**, 328.
[5] Ibid. **219**, 363.

[6] Michael and Norton, this Journal **2**, 15; also Erlenmeyer and Müller (Berichte d. deutsch. chem. Gesell. **15**, 49), who subsequently showed that a small amount of alpha-acid is formed at the same time.

[7] That the importance of these observations was not overlooked will be seen from the follow-ing extract: "The formation of different bromcrotonic acids from α- and $\alpha\beta$-dibrombutyric acids presents considerable interest, as Tollens has shown that the α- and $\alpha\beta$-dibrompropionic acids yield the same bromacrylic acid. Our results, in thus characterising an important diff-erence in the properties of substitution products of propionic and butyric acids, indicate that a more thorough and systematic investigation than has hitherto been made of the substitution products of the fatty acids will show further marked differences in the properties of these acids ; results which would contribute in no small measure to a better insight into the relations and nature of homologous organic compounds." This Journal **2**, 20.

Addition of Bromhydric Acid to Tetrolic Acid.

If the bromcrotonic acid obtained from *α,β*-dibrombutyric acid is the *β*-derivative of solid crotonic acid, its synthesis should be realised by the addition of bromhydric acid to tetrolic acid, as the halogen in these reactions always takes the *β*-position towards the carboxyl, and besides it has been proved that tetrolic and chlorhydric acids unite to form *β*-chlorcrotonic acid.[1]

In preparing bromcrotonic acid from tetrolic acid it is necessary to start from the latter acid in a perfectly pure state. Our first experiments were made with an acid that had the correct melting point, but gave a faint trace of halogen when heated in a flame with copper oxide. This acid was sealed in a tube with a large excess of bromhydric acid (saturated at 0°), and kept cool for about a day. On addition of water to the solution, long white needles separated that in a crude state melted from 75°–83°; after several crystallisations from water, at 83°–85°; but repeated crystallisation from ligroin brought the substance to the constant melting point of 94°–95°. The bromine estimations of this apparently pure substance gave results that were over one-half per cent. less than that indicated by theory, and a silver estimation of the silver salt came somewhat more than two per cent. higher than the theoretical percentage. It seems very probable from these results that the chlorcrotonic acid contained in the tetrolic acid has very nearly the solubility of the bromcrotonic acid formed in the reaction, and cannot be separated from it by crystallisation.

The difficulty is obviated by starting with perfectly pure tetrolic acid, and we found that working according to the following directions gave the most satisfactory results: A mixture of one part of tetrolic acid and five parts of bromhydric acid, saturated at 0°, is sealed in a glass tube, placed on ice for about five hours, and then allowed to stand at ordinary room-temperature for two or three days. It was noticed that tetrolic acid dissolves immediately in bromhydric acid, and that after several hours long needles begin to separate from the solution. The contents of the tube is mixed with an equal volume of water, cooled off in ice, and the precipitate separated by filtration. The precipitate melted from 75°–83°; repeated crystallisation from water failed to raise the melting point above 85°, but after crystallising it four times

[1] Friedrich, Annalen der Chemie **219,** 370.

from ligroin it melted constantly at 94.5°–95°. The analyses of this product gave the following figures:

0.3606 gram substance dried in a vacuum gave 0.3829 gram CO_2 and 0.1116 gram H_2O.

0.2193 gram substance dried in a vacuum gave 0.2517 gram AgBr.

	Theory for $C_4H_5BrO_2$.	Found.
C	28.96	29.09
H	3.43	3.03
Br	48.84	48.48

The new bromcrotonic acid crystallises from water as cuneated plates; from ligroin in firm feathery needles that melt at 94.5°–95°. It is sparingly soluble in cold, pretty soluble in hot water, and separates from its warm aqueous solution on cooling as an oil that solidifies on standing. In cold ligroin it is sparingly soluble, but readily soluble in cold benzene, carbon bisulphide, acetic ether, acetic acid, ether, alcohol, and chloroform. Treated with steam the acid passes over with difficulty. The formation of this acid is represented by the following equation:

$$CH_3 — C — C — COOH + HBr = CH_3 — CBr — CH — COOH.$$
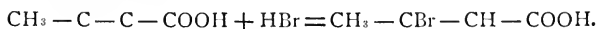
The potassium salt was obtained by neutralising an aqueous solution of the acid with pure caustic potash, and allowing the solution to evaporate by exposure to the air until most of the salt had separated. It is filtered from the mother liquor, washed with alcohol, and dried by exposure to the air. The salt crystallises as thin plates that are readily soluble in cold water and do not contain water of crystallisation.

0.8140 gram air-dried salt did not lose in weight when heated to 100°, and gave 0.3469 gram K_2SO_4.

	Theory for $CH_3 — CBr — CH — COOK$.	Found.
K	19.13	19.21

The silver salt was made by precipitating an aqueous solution of the potassium salt with silver nitrate, filtering the precipitate, and crystallising it from water. It crystallises in thin white, almost opaque plates that are moderately sensitive to the action of light. It does not contain water of crystallisation.

0.4107 gram air-dried salt did not change its weight at 100°, and gave 0.288 gram AgBr.

	Theory for $CH_3 — CBr — CH — COOAg$.	Found.
Ag	39.70	40.33

The barium salt was obtained by adding an excess of barium carbonate to an aqueous solution of the acid, allowing the mixture to stand for an hour, filtering, and concentrating the filtrate by evaporation at ordinary temperature. It crystallises in colorless plates and prisms that are readily soluble in water and insoluble in hot absolute alcohol. They contain one molecule of water of crystallisation.

0.4285 gram air-dried salt lost 0.0172 gram H_2O at 100°.

0.5768 gram air-dried salt gave 0.2812 gram $BaSO_4$.

0.5078 gram air-dried salt gave 0.2465 gram $BaSO_4$.

0.3422 gram salt dried at 100° gave 0.1742 gram $BaSO_4$.

	Theory for $(CH_3-CBr-CH-COO)_2Ba.H_2O.$	Found.	
H_2O	3.73	4.01	
Ba	28.36	28.66	28.56

	Theory for $(CH_3-CBr-CH-COO)_2Ba.$	Found.
Ba	29.46	29.89

The properties of the three known bromcrotonic acids are given below in tabular form.

a-*Acid*.	aλ-a-*Acid* (*old* β).	β-*Acid*.
From $CH_3-CH_2-CBr_2-$ COOH. Long needles (from water). Needles that can be easily pulverised (from ligroin).	From $CH_3-CHBr-CHBr-$ COOH. Long needles. Needles that can be easily pulverised.	From $CH_3-C-C-COOH$ and HBr. Cuneated plates. Firm feathery crystals that can only be pulverised with difficulty.
Melting point 106.5°.	90° (C. Kolhe). 92° (Michael and Norton).	94.5°-95°.
Silver Salt.		
White needles. Stable towards light.	White needles. Very sensitive to light. Cannot be crystallised from water without decomposition.	Thin plates. Moderately sensitive to light. Can be crystallised from water.
Barium Salt.		
Plates, with two molecules of water of crystallisation.	Plates, with 3½ molecules of water of crystallisation.	Prisms, with one molecule of water of crystallisation.

It semed possible to obtain a second β-bromcrotonic acid by allowing phosphorus pentabromide to act on acetacetic ether; as, if the reaction takes place analogously to that of the pentachloride on the ether, a mixture of two β-acids should be formed. To 50 grams acetacetic ether 330 grams powdered pentabromide were gradually added. The liquid, which had a deep violet color, was poured in small portions into cold water, and the solution shaken out with ether. After evaporating the ether the residue was treated with steam, but the quantity of acid that passed over was

too small to permit its investigation. The residue remaining after steaming was crystallised from water, and then six times from ligroin, when it gave a constant melting point of 85°. A bromine estimation of the acid gave 29.13 per cent. bromine, a result that showed the reaction had not taken place in the way that was expected, as bromcrotonic acid contains 48.8 per cent. of bromine. The product was not further examined.

Behavior of α,β-Dibrombutyric Ethylether towards Alkalies.

The observation made by one of us that α,β-dibromhydrocin-namic acid when decomposed by alkalies gives a different result from that given by the ether of the acid[1] led us to examine the bromcrotonic acid formed by decomposing α,β-dibrombutyric ether with alkalies. In decomposing α,β-dibrombutyric acid about nine-tenths of the bromcrotonic acids formed consists of allo-α-acid (old β-acid), and the remaining tenth of α-acid.

The ether was made by saturating a solution of one part of α,β-dibrombutyric acid in three parts of absolute alcohol with dry chlorhydric acid, at first without outward cooling, and then cooling at 0°. After standing twenty-four hours the liquid was poured into cold water, the mixture extracted with ether, and the ethereal solution, after shaking out with aqueous sodium carbonate, dried over calcium chloride. On evaporation of the ether the residue was distilled in a vacuum (30 mm. pressure, bath at 160°), when the greater part passed over from 110°–115°, and several fractiona-tions under the same conditions of pressure gave an oil boiling constantly at 113°–114°. The analysis of this oil gave figures as follows :

0.1780 gram oil gave 0.2405 gram AgBr.
0.2132 gram oil gave 0.2893 gram AgBr.

	Theory for $CH_3 - CHBr - CHBr - COOC_2H_5$.	Found.	
Br	58.39	57.50	57.74

[1] These observations, which I made about a year ago, have never been published. According-ing to Glaser (Annalen der Chemie **154**, 146), allo-α-bromcinnamic acid is formed in the decomposition of αβ-dibromhydrocinnamic acid in much greater proportion than the α-acid. In making bromcinnamic acids from αβ-dibromhydrocinnamic ether I noticed that the relative proportions of bromcinnamic acids that are formed are reversed. In this case the α-acid forms the principal product, while the allo-a-acid is formed in much smaller quantity. These facts explain why the ether can be used to greater advantage for preparing phenylpropiolic acid than the acid.—A. M.

The ether forms a colorless heavy oil that boils in a vacuum (30 mm., oil-bath 150°) without decomposition at 113°. The ether was dissolved in a small amount of alcohol, and alcoholic caustic potash (one molecule of ether to two molecules of alkali) added. A violent reaction took place, and an immediate deposition of potassium bromide was noticed. After heating several minutes on a water-bath the alcohol was evaporated, and the residue extracted with cold absolute alcohol. It was filtered, the precipitate dissolved in water, and the solution acidulated and extracted with ether. On evaporation of the ether a large amount of nearly pure α-bromcrotonic acid was left. After one crystallisation it gave the correct melting point (106°). The absolute alcoholic extract contained a small amount of a potassium salt, but whether any αλ-α-bromcrotonic is formed from α,β-dibrombutyric ether we are unable at present to ascertain. The experiment will be repeated on a larger scale with this object in view. It is certain, however, that α-bromcrotonic acid is the main product of the reaction, a result which is exactly the reverse of that obtained in decomposing the free acid.

Addition of Chlorine to Solid Crotonic Acid.

The behavior of solid crotonic acid towards chlorine was examined by Friedrich,[1] who passed the dry gas into the acid, and obtained a liquid addition product that could not be brought into a solid state. No analyses of the product are given. As Friedrich noticed the formation of chlorhydric acid in the operation, the reaction was evidently too energetic, and we therefore used a solution of the acid in carbon disulphide. We experienced, however, considerable difficulty in ascertaining the proper conditions, as will be noticed from the following experiments.

Five grams crotonic acid were dissolved in four hundred grams carbon bisulphide, and the solution saturated by a slow current of dry chlorine, an operation that took about five hours. A portion of this solution was heated on a water-bath until the carbon bisulphide was expelled, and the residue was found to consist of unchanged crotonic acid. A second portion was exposed to sunlight for a few hours, when a slight addition took place, but the greater part of the crotonic acid remained unchanged. The remainder of

[1] Annalen der Chemie **219**, 368.

the solution was allowed to stand in the cold for a day, and the bisulphide then evaporated. The residue melted at 59°–60°, and after repeated crystallisation from ligroin at 60°–60.5°. A chlorine estimation of this product gave 35.42 per cent. Cl, which is nearly ten per cent. below the calculated chlorine of dichlorbutyric acid. Three grams crotonic acid were dissolved in one hundred grams chloroform, and the solution saturated with chlorine. After four days the chloroform was evaporated, but the residue remained an oil, and could not be purified by fractionation. Three grams acid in one hundred grams chloroform and four and a half grams iodine were treated with chlorine until saturation. Iodine trichloride separated, and apparently did not act on the acid.

A solution of five grams crotonic acid in four hundred grams carbon bisulphide was cooled to —17°, and saturated with chlorine at that temperature. After standing a week in a cool place a portion was worked up, and gave a solid product melting at 57.5°–58°, and containing 43.69 per cent. Cl (theory 45.22). The remainder was again saturated with chlorine at —17° and allowed to stand several days. In this manner we obtained a product melting at 63° and consisting of pure dichlorbutyric acid.

We give the following directions as the results of our experience in preparing the acid. Ten grams crotonic acid are dissolved in four hundred grams dry carbon bisulphide, the solution cooled in a mixture of ice and salt, and saturated with dry chlorine. It is kept in a cool place for three days, then resaturated with chlorine under the same conditions, allowed to stand several days, and the carbon bisulphide evaporated by heating on a water-bath. There remains a thick heavy oil which contains a considerable amount of chloride of sulphur. The mass is treated with an excess of aqueous sodium carbonate, the solution filtered, and then, after acidifying, extracted with ether. The ethereal solution is dried over calcium chloride, and leaves, on evaporating the ether, a thick oil that deposits prismatic crystals on standing. These are separated by filtration, crystallised once from ether and several times from ligroin.

0.2672 gram acid gave 0.4854 gram AgCl.

	Theory for $CH_3 - CHCl - CHCl - COOH$.	Found.
Cl	45.22	44.92

The acid crystallises in thick white prisms that are somewhat

deliquescent and melt at 63°. It is very soluble in benzene, ether, chloroform, carbon bisulphide, and hot ligroin, sparingly soluble in cold ligroin and cold water. It is evident that Friedrich worked with an impure acid.

Behavior of αβ-Dichlorbutyric Acid towards Alkalies.

The acid was dissolved in a small amount of alcohol, and an alcoholic solution of caustic potash (one molecule of acid to two molecules of base) gradually added. The reaction is energetic, but the solution was kept below 40° C. by cooling. After the solution became neutral it was mixed with water, acidified, and extracted with ether. The extract, after drying over calcium chloride, was heated on a water-bath until the ether was expelled, and the residue on cooling solidified to a crystalline mass. This was purified by crystallisation from water and ligroin, and gave the following results on analysis:

0.2348 gram substance gave 0.3481 gram CO_2 and 0.1018 gram H_2O.

0.2113 gram substance gave 0.3141 gram CO_2 and 0.0930 gram H_2O.

0.2285 gram substance gave 0.2728 gram AgCl.

0.2159 gram substance gave 0.2574 gram AgCl.

	Theory for $CH_3-CH-CCl-COOH.$	Found.	
C	39.83	40.43	40.54
H	4.15	4.81	4.89
Cl	29.46	29.53	29.48

The new chlorcrotonic acid crystallises from water, ligroin, or ether in fine needles that melt at 67°. It is readily soluble in hot, sparingly in cold ligroin. In warm water it is readily, in cold moderately soluble, but more so than any of the three isomeric chlorcrotonic acids, as is evident from the following determinations of solubilities:

12 grams of a saturated aqueous solution of the new acid at 19° required 75.7 cc. of caustic potash solution containing 0.0004817 gram KOH in a cc.

12.55 grams of a saturated aqueous solution of α-chlorcrotonic acid (97°) at 19° required 25.6 cc. of caustic potash solution containing 0.0004817 gram KOH in a cc.

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12.1 grams of a saturated aqueous solution of β-chlorisocrotonic acid (59°) at 19° required 22.6 cc. of caustic potash solution containing 0.0004817 gram KOH in a cc.

From these results the following solubilities were calculated :

15.3 grams water at 19° dissolve one gram new chlorcrotonic acid.

47.1 grams water at 19° dissolve one gram a-chlorcrotonic acid.

52.4 grams water at 19° dissolve one gram β-chlorisocrotonic acid.

It will be noticed that the new acid is above three times more soluble in water than either of the two isomeric acids, and it is more soluble than the fourth isomeride, as that acid dissolves in 44 parts of water at 12.5°.[1]

To obtain the potassium salt an aqueous solution of the acid was neutralised with caustic potash, and the solution evaporated by standing in the air. The crystals were filtered, washed with absolute alcohol, and dried by exposure to the air. It is easily soluble in water, moderately in absolute alcohol, and crystallises from that solvent in concentric groups of fine needles. The salt does not contain water of crystallisation.

0.4318 gram salt dried by exposure to the air underwent no change in weight at 100°, and gave 0.2352 gram K_2SO_4.

	Theory for $CH_3 - CH - CCl - COOK.$	Found.
K	24.60	24.45

The barium salt was made by neutralising an aqueous solution of the acid with barium carbonate, and evaporating the filtered solution at ordinary temperature on the air. It is a white crystalline salt that is easily soluble in water, but slightly soluble in alcohol, and contains three and a half molecules of water of crystallisation.

0.6922 gram air-dried salt lost 0.0976 gram H_2O at 125° C.

0.5946 gram salt dried at 125° gave 0.3678 gram $BaSO_4$.

	Calculated for $(CH_3 - CH - CCl - COO)_2Ba.3H_2O.$	Found.
H_2O	14.35	14.10
	Calculated for $(CH_3 - CH - CCl - COO)_2Ba.$	Found.
Ba	36.43	36.37

By adding a solution of lead nitrate to a solution of the potassium salt a crystalline precipitate was deposited that was

[1] Kahlbaum, Berichte d. deutsch. chem. Gesell. **12**, 2339.

crystallised from water. It forms white, vitreous, prismatic needles or short prisms that are somewhat soluble in water and contain one molecule of water of crystallisation.

0.3063 gram salt dried by exposure to the air lost 0.116 gram H_2O at 100° C.

	Theory for $(C_4H_4ClO_2)_2Pb.H_2O$.	Found.
H_2O	3.87	3.78

0.2947 gram salt dried at 100° C. gave 0.2002 gram $PbSO_4$.

	Calculated for $(C_4H_4ClO_2)_2Pb$.	Found.
Pb	46.41	46.43

On addition of silver nitrate to a solution of the potassium salt, a silver salt is precipitated as a white amorphous compound that is somewhat soluble in water, and not very stable on exposure to light.

The sodium salt, obtained by neutralising the acid with caustic soda and evaporating, forms small prismatic needles that are easily soluble in alcohol.

A solution of copper sulphate added to a solution of the potassium salt gives a precipitate of greenish-blue, concentrically grouped prisms that are difficultly soluble in water.

Behavior of αβ-Dichlorbutyric Ether towards Alkalies.

It seemed of interest to ascertain whether the ether of αβ-dichlorbutyric acid would yield on treating with alkalies the same chlorcrotonic acid as the free acid ; or whether, as is the case with the dibrombutyric and hydrocinnamic acids, an isomeric alpha-acid would be formed in the reaction.

Pure αβ-dichlorbutyric acid in absolute alcoholic solution was saturated with dry chlorhydric acid. The solution was then allowed to stand about twelve hours, thrown into cold water, and extracted with ether. The ethereal solution was extracted with a dilute solution of sodium carbonate, dried over calcium chloride, and, after evaporation of the ether on a water-bath, fractionated in a vacuum. In this manner a colorless oil was separated that boiled under 35 mm. pressure at 96° (oil-bath at 145°).

0.2312 gram ether gave 0.3581 gram AgCl.

	Theory for $CH_3 - CHCl - CHCl - COOC_2H_5$.	Found.
Cl	38.91	38.30

A portion of dichlorbutyric ether was dissolved in alcoholic potash, in the proportion of one molecule ether to two molecules alkali, and the solution allowed to stand in the cold for three or four hours. It was then worked up in the manner already described in the decomposition of dibrombutyric ether, and the chlorcrotonic acid obtained in this way consisted of the a-acid melting at $97°-98°$.

We meet in this case the same remarkable difference in the behavior of a,β-dichlorbutyric acid and its ether towards alkalies as already proved with the corresponding bromo-compounds. While free a,β-dichlorbutyric acid and alkalies give an a-chlorcrotonic acid melting at $67°$, the ether of the same acid when decomposed by alkalies gives the alloisomeric a-chlorcrotonic acid melting at $98°$.

By-product formed in the Addition of Chlorine to Solid Crotonic Acid.

In the preparation of a,β-dichlorbutyric acid mention was made of an oil from which the solid acid separates and which does not solidify further on long standing. A small quantity of the solid addition product may be obtained by allowing the oil to stand in a vacuum over sulphuric acid for a number of days, when it separates in large crystals ; the greater part of the oil, however, could not be brought into a solid state. We endeavored to purify this oil, which is an acid, by fractionation in a vacuum, but it decomposed in the operation. A second portion was then treated in alcoholic solution with chlorhydric acid, and the ether thus obtained fractionated in a vacuum. In this manner it was easy to obtain a good yield of a colorless oil that boiled at $93°$ under 30 mm. pressure (oil-bath $145°-150°$). This oil agreed in its properties with a,β-dichlorbutyric ether, but the analyses showed that it contained a small amount of an impurity that could not be separated by fractionation, as the chlorine estimations were from 1.2 to 1.5 per cent. below those indicated by theory. That it consisted largely of a,β-dichlorbutyric ether was further confirmed by its behavior toward alkalies. Six grams oil were treated with alcoholic potash and the mixture allowed to stand for several hours. The precipitate was dissolved in water, acidified, and the solution extracted with ether. On evaporation of the ether, a-chlorcrotonic acid melting at $97°-98°$ was obtained. The alcoholic filtrate was

worked up for chlorcrotonic acid, and was found to contain a very small amount of allo-*a*-acid melting at 67°.

To judge from these experiments it seems probable that the oil consisted largely of *aβ*-dichlorbutyric acid which was prevented by some impurity from solidifying.[1]

Remarks on the Preceding Experiments.

The constitutions of two of the three known bromcrotonic acids may be regarded as hardly open to doubt. If, as seems reasonably certain, *a*-dibrombutyric acid has the constitution generally assigned to it, then *a*-bromcrotonic acid (106°), obtained from it by elimination of bromhydric acid, can have no other constitution than $CH_3 — CH — CBr — COOH$. In regard to the new acid formed by addition of bromhydric acid to tetrolic acid, it is safe to assume, relying on the rule that the halogen takes the *β*-position towards carboxyl which is true without any exception,[2] and that chlorhydric acid unites with tetrolic acid to form *β*-chlorcrotonic acid, that we have in this acid a *β*-bromcrotonic acid of the constitution $CH_3 — CBr — CH — COOH$. The formation of the third bromcrotonic from *aβ*-dibrombutyric acid admits of three different interpretations :

$$\text{CH}_3\text{-CHBr-CHBr-COOH} = \begin{cases} \text{I. CH}_3\text{-CH-CBr-COOH} + \text{HBr} \\ \text{II. CH}_3\text{-CBr-CH-COOH} + \text{HBr} \\ \text{III. CH}_2\text{-CH-CHBr-COOH} + \text{HBr} \end{cases}$$
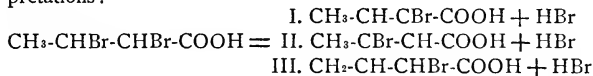
Of these three formulae those marked as I and II are impossible for the acid, as acids of these constitutions have been obtained by different methods and found to be different from the acid in question. There remains, assuming for the moment the impossibility of two chemical isomerides being represented by the same structural formula, the formula marked III, and we shall briefly consider whether there are any reasons for assigning this constitution to the third acid.

[1] We subsequently succeeded in obtaining *aβ*-dichlorbutyric acid from this ether. It was gently heated in an open vessel with strong chlorhydric acid for several hours, and the solution extracted with ether. After drying over calcium chloride the ether was evaporated, and the residue placed in a vacuum over sulphuric acid, when it gradually solidified, and the solid substance was found to be identical with *aβ*-dichlorbutyric acid.

[2] According to Hemilian (Annalen der Chemie **174**, 326), hydriodic and bromhydric acids form principally *a*-addition products besides small quantities of *β*-acids. This view is based on a misconception of the behavior of *β*-halogen acids towards reagents, and, as we shall show in another paper, the relative proportions of *a*- and *β*-acids formed in the reaction should be reversed.

The influence of carboxyl on the hydrogen of an organic acid shows itself primarily on those of the adjacent carbon in making these hydrogen more reactive, or, in other words, loosening its affinity to carbon. This is the reason why the a-hydrogen of an acid are those that enter into chemical reactions in preference to the hydrogen of the following carbons, and that β-halogen acids decompose with such great facility into unsaturated acids and halhydric acids, in contradistinction to the behavior of a-derivatives, that, owing to the greater affinity of hydrogen for carbon in the β-position, decompose with difficulty, and generally form substitution products instead of unsaturated acids. While it is safe to follow the relation between chemical structure and properties as indicated by the present structural formulae as far as hydrocarbon radicals in the a- and β-position towards carboxyl are concerned, any assumption in regard to the relation between carboxyl and such radicals in other positions must for the present be regarded as dogmatic, as the present hypotheses do not show this connection further than the β-position. We may assume, however, that carboxyl does not influence in a marked degree the hydrogen of a hydrocarbon radical in the γ-position, as in no case have γ-derivatives been found among the products formed in the action of halogens on such acids, nor have these hydrogen entered in reactions involving condensations or polymerisations. For these reasons it is theoretically improbable that in the formation of the third bromcrotonic acid from a,β-dibrombutyric acid, γ-hydrogen and β-bromine should be those that are eliminated. If we judge from analogous reactions it is a-hydrogen and β-bromine that split off, as a,β-dibrompropionic acid forms a-bromacrylic, and a,β-dibromhydrocinnamic forms two alloisomeric a-bromcinnamic acids under the same conditions. We believe that the only probable structural formula for the third bromcrotonic acid is that already assigned to a-bromcrotonic acid, and, to distinguish it from that compound, we have called it allo-alpha-bromcrotonic acid, a name indicating that the acid is the a-derivative of allocrotonic acid. It is particularly the remarkable differences noticed in decomposing a,β-dibrombutyric acid and its ethyl ether that show the improbability of the third acid having the constitution $CH_2 - CH - CHBr - COOH$. We can hardly imagine that the ether should lose β-halogen and a-hydrogen, as has been shown by the formation of a-bromcrotonic acid from it, while the free acid should not lose halogen and

hydrogen in a similar manner.[1] These are in fact reactions that show how totally inadequate the present hypotheses are to explain or represent the formation of alloisomeric compounds.

These views apply with equal force to the constitution of the chloro-crotonic acids. The formation of a-chlorcrotonic acid (98°) from $a\beta$-dichlorbutyric ether proves that this acid corresponds in its constitution to the a-bromcrotonic acid (106°) obtained from $a\beta$-dibrombutyric ether and a-dibrombutyric acid, and the new chlorcrotonic acid can have no other constitution than that of an $a\lambda$-a-chlorcrotonic acid, represented by the same structural formula as the a-chlorcrotonic acid.

It is unnecessary to make more than a brief mention of the improbability of β-chlorallocrotonic acid having the constitution $CH_2 - CCl - CH_2 - COOH$. This view assumes the elimination of γ-hydrogen, which directly contradicts everything that is known regarding the influence of carboxyl on the hydrogen of organic acids. The formation of two acids in the action of phosphorus pentachloride on acetacetic ether possibly stands in connection with the formation of different halogen-crotonic acids from an ether or the free acid. One of the chlorcrotonic acids may be formed by elimination of chlorhydric acid from the chloride of β-dichlorbutyric acid, when the second acid is formed from the ether of that acid.[2]

In view of the results described in this paper, as well as in our papers on the bromcinnamic acids, it is necessary to change the law on the decomposition of $a\beta$-halogen acids as stated by Erlenmeyer.[3] According to that chemist, a-halogen and β-hydrogen are principally eliminated, but a secondary reaction takes place, in which β-halogen and a-hydrogen are split off. This law cannot be longer upheld, and must be modified to read that when two halogen acids are formed in the decomposition of an $a\beta$-dihalogen acid, both these products are a-derivatives of alloisomeric acids, and when but one acid is formed, the acid is an a-derivative.

TUFTS COLLEGE, MASS.

[1] It is probable that the tribrombutyric acids obtained from a- and $a\lambda$-a-bromcrotonic acid by addition of bromine are identical. We intend to repeat these experiments, and also to make a thorough examination of the brom- and chlorcrotonic acids with a view of bringing further proofs of the constitutions of the compounds presented in this paper.

[2] We intend to make a thorough comparative examination of the behavior of halogen acids and their ethers towards alkalies, to ascertain whether the differences that were observed between dibrombutyric, hydrocinnamic, and dichlorbutyric acids and their ethers towards alkalies represent a general law. This investigation promises to open a very interesting field of research, and we should like to reserve the continuation of our observations on this subject until the work is completed.

[3] Berichte d. deutsch. chem. Gesell. **15**, 49.

X.—THE ESTIMATION OF CARBONIC ACID IN BEER.

By C. A. CRAMPTON AND T. C. TRESCOT.

Most analysts have given very little attention to the determination of the carbonic acid in malt liquors, regarding it as of but little importance in forming an estimate of the quality of the sample examined. The practical consumer, however, is of quite a different opinion, and condemns immediately a beer which is "flat" or insufficiently carbonated, however worthy it may be in other respects. The reason for its importance as a determination is found in the difficulty of its accurate estimation in the beer as supplied to the consumer. The usual method of determining it is to measure or weigh out a convenient quantity of the beer into a flask, connect the latter either with an absorbing apparatus for the estimation of the carbonic acid direct, or with a suitable apparatus for the retention of watery vapor, thus estimating it by loss, or indirectly; its liberation being accomplished in either case by a low degree of heat. But this manner of manipulation gives simply the amount of carbonic acid capable of being held in solution by a liquid of the density and temperature of the beer when it was measured out, supposing it to have been fully charged previously. The excess of gas above the saturation point, however, which is held by the beer so long as it is kept under pressure or at a low temperature, escapes as soon as the pressure is removed, and gives the beer its "head," which is so desirable a qualification. This excess of gas soon passes off after it is drawn from a cask, or a bottle opened, but in this short interval the beer is drank. The problem is to estimate the carbonic acid just as it exists in the beer before consumption. This is a difficult matter with beer contained in casks or kegs, though it might be accomplished by drawing a sample off by means of gas-tight connections, as in gas analysis. But where the beer is furnished in stoppered bottles it is an easy matter, and furnishes a most valuable index as to the freshness and proper preparation of the beer. Where secondary fermentation or souring has set in there will be an excess of carbonic acid, and the beer will have become turbid. Where there is a good content of carbonic acid, but the acidity of the beer is very low, the indications are that bicarbonate of soda has been added.
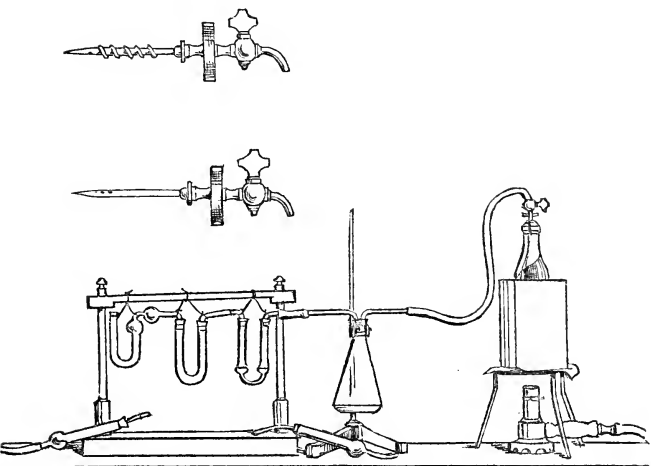
In the course of an investigation of the composition and extent of adulteration of the beers sold in this country we had occasion to devise a form of apparatus to accomplish this purpose. Hassall speaks of the estimation of carbonic acid in bottled aerated waters, the gas being drawn by means of a champagne tap, and Dr. Wiley[1] has estimated the carbonic acid in koumiss in that way, using a calcium chloride tube for the retention of the water carried off by the gas, and estimating it by difference, the whole bottle being weighed. In applying this form of apparatus to beer we experienced considerable difficulty on account of the viscosity of the liquid. The bubbles formed were so tenacious that when the bottle was connected directly with a calcium chloride or sulphuric acid tube, the latter would become filled with the beer in a very short time. This difficulty was obviated by the use of the form of apparatus shown in the cut. The cork of the bottle is pierced with a champagne tap, and this is connected with an Erlenmeyer flask, in the broad bottom of which the bubbles are broken and not allowed to pass beyond it; next comes a U-tube filled with sulphuric acid,

[1] This Journal **8**, 200; Ann. Rept. U. S. Dept. Agr. 1886, 118.

then a calcium chloride tube, then a soda-lime tube to absorb the dried carbonic acid. The bottle of beer is placed in a convenient vessel—an empty ether can with the top cut off answers admirably, as in the cut—which is nearly filled with cold water. After the apparatus is connected the tap is opened slowly and the gas allowed to flow through the apparatus. When it ceases to flow spontaneously, a lamp is placed under the can and the temperature gradually raised until it reaches 80° C., beyond which it should not be carried. By keeping it at this temperature for about half an hour and taking the bottle out and shaking it occasionally, all the carbonic acid may be driven off. Then the tube from a suction pump is connected with a calcium chloride tube, and this in turn with the soda-lime tube. The valve of the tap is then closed, the latter removed from the bottle, connected with a soda-lime tube, and by gradually opening the valve a stream of air from which the carbonic acid has been removed is drawn through the apparatus by the pump, so that all the carbonic acid contained in it is drawn into the soda-lime tube and absorbed. The increase in weight of the latter, of course, gives the amount of carbonic acid in the beer. The quantity of the latter is measured or weighed, that which has been carried into the Erlenmeyer flask being added. In the case of large bottles it may be found necessary to add a second soda-lime tube, and it is best to use fresh soda lime for each determination. It was found necessary to modify the champagne taps used, for the thin-edged thread with which they are provided cuts the cork too much and allows the escape of the gas. Accordingly this thread was turned off entirely, leaving a smooth tube, as shown in the accompanying figures. This can be forced through the cork with little difficulty, and allows no leakage of gas. It was also found necessary to have the cock reground to make it fit accurately.

The patent rubber-stoppered beer bottles presented a difficulty in this method of analysis, as it was impossible to make a gas-tight connection with them without the escape of the confined gas. In these the gas was estimated by loss in weight, calcium chloride and sulphuric acid tubes and connections being weighed with the bottle on a large balance, the bottle opened and connections made as soon as possible, the gas driven off as before, and the loss ascertained by weighing the entire apparatus again. It is necessary to raise the heat very gradually to prevent the filling up of the tubes with the beer carried over by the bubbles. There is a slight error from

the watery vapor which escapes with the pressure of gas when the bottle is opened, and altogether the determination is not so satisfactory as with the cork-stoppered bottles. Analyses of bottled beers made in this way gave much higher results than are given in the books, as the following table shows.

No.	Per cent. CO_2.	No.	Per cent. CO_2.
1	.411	10	.629
2	.300	11	.344
3	.489	12	.503
4	.415	13	.397
5	.328	14	.441
6	.471	15	.592
7	.717	16	.242
8	.219	17	.265
9	.324		

Nos. 1, 3, 4 and 7 had rubber stoppers, the rest cork. No. 7 was evidently in a state of after fermentation, cloudy and acid; excluding that analysis, the 16 others give an average of .398 per cent.; most authorities give an average of .1 to .2 per cent. in beer.

In Nos. 2 and 5 duplicate analyses were made with different bottles of the same lot, with the following results:

	I.	II.
No. 2	.294	.307
No. 5	.329	.327

A sample of bottled cider which had evidently been manufactured, as shown by other tests, gave in different bottles the following numbers:

I.	II.	III.
.728	.654	.482

Bicarbonate of soda had probably been added to each bottle in varying amount. It is likely that in all cases of bottled ciders where the content of carbonic acid is very high, that it has been added to the cider in some way, for cider that has been racked and cleared, fit for bottling, contains very little carbonic acid, barely enough to give it a slight sparkle. This is a matter for further investigation. Two samples of "champagne cider" analysed by us gave the following per cent. of CO_2: .161, .120.

AN IMPROVED FORM OF ELLIOTT'S GAS APPARATUS.

By J. B. Mackintosh.

In the ordinary form of this apparatus as described by Elliott,[1] the transfer of the residual gases from the absorption apparatus to the explosion burette is attended with some difficulty and with the liability of accidentally introducing some air during the operation unless great care be taken. In order to obviate these troubles and, incidentally, also to diminish the number of loose pieces, I have devised the simple modification shown in the illustration. The essential feature is the three-way T-stopcock on the measuring burette, whereby connection may be made between any two of the burettes, to the complete isolation of the other. Another time-saving device is in the fixing of the zero points of the graduations. In the measuring and explosion burettes the zero point O is taken at that point where the capillary tube expands into the burette, and where the water will naturally remain when the excess drains to the bottom of the burette. This renders the adjustment to zero an automatic one, with no sacrifice of accuracy. The absorption tube has a single graduation at 100 cc. measured from the point A. In filling this tube with gas to the mark, a small quantity remains in the portion of the tube above A, but this may be removed by first closing the lower stopcock S and then forcing water out of one of the other burettes. This slightly compresses the gas in the absorption tube, and at the same time expels the excess, so that we then have exactly 100 cc. at the atmospheric pressure.

In transferring gas to the explosion burette from the measuring tube, the portion remaining in the capillary tube and in the ways of the T-stopcock is removed by passing water from the absorption tube, preferably by letting it flow in from the funnel. The T-stopcock being then turned so as to connect the explosion and absorption tubes, the gas remaining in the measuring tube is perfectly isolated, and none of it has been lost during the transfer. We are now ready to introduce oxygen and air for the explosion, which may be done either as Elliott directs, through the lower stopcock of the explosion burette, or through the funnel of the absorption tube, or both.

[1] School of Mines Quarterly **3**, 16, and **4**, 322; and Chemical News, October, 1883.
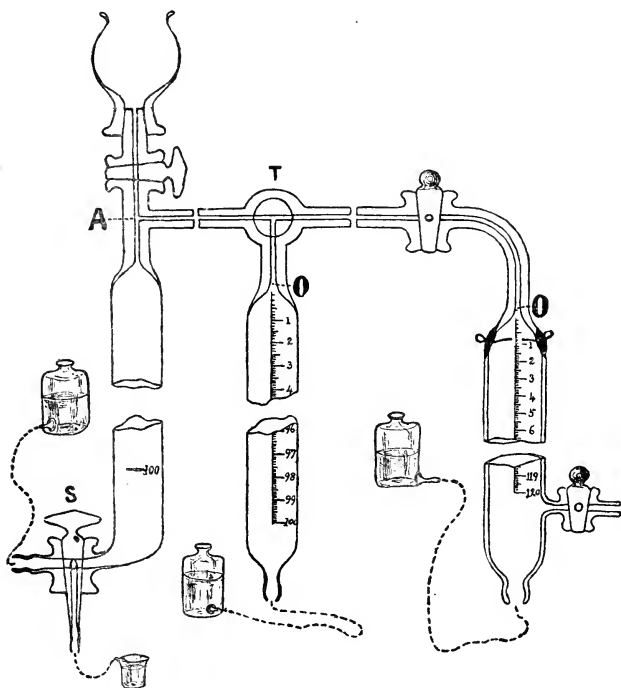
In case we have not a store of oxygen under pressure for use, I have found that a very convenient source of this indispensable reagent is available in the reaction of peroxide of hydrogen on acidified solution of potassium permanganate. We can thus manufacture in the absorption tube as much pure oxygen as we need, by first running in some permanganate, then the peroxide of hydrogen, and then more permanganate, until we have added enough to decompose all the peroxide taken. We then wash the permanganate out of the funnel, etc., with water, pass as much oxygen as we need into the explosion burette, empty the capillary tube of oxygen as before by letting water run in from the funnel, and, finally, empty and wash out the absorption tube and make it

in readiness for the absorption of the carbonic acid resulting from explosion. Air may now be introduced in sufficient quantity, and after mixing the gases by removing and inclining the burette, the explosion may be made, the contraction noted, the gas transferred to the absorption burette, and the carbonic acid absorbed, and, finally, retransferred to the explosion burette and the residual gas measured.

The apparatus as figured was made for me by Mr. Emil Greiner of 79 Nassau Street, New York, to whose good workmanship I am pleased to render tribute.

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A NEW PYROMETER.

BY E. H. KEISER.

New methods for the determination of high temperatures have recently been described by Justus Mensching and Victor Meyer,[1] and by L. F. Nilson and Otto Pettersson.[2] In both cases the apparatus is constructed for the double purpose of measuring high temperatures and making vapor density determinations. Excellent as these methods are, a single temperature determination by either one of them requires the employment of a complicated system of apparatus, and must undoubtedly take considerable time. In chemical laboratories it is, however, frequently necessary to determine melting and boiling points which lie above 360° C. It is therefore very desirable to have a simple form of air thermometer by means of which these high temperatures may be rapidly and accurately determined. The following is a description of an apparatus which fulfills these conditions and which has given satisfactory results in my laboratory.

The pyrometer consists of two parts, the bulb A and the eudiometer B. The vessel A has a capacity of about 100 cubic centimeters. It is closed at one end, and to the other end is attached a capillary stem which is from 20 to 25 centimeters in length. For measuring temperatures below the melting point of glass this bulb may be made of hard glass. For higher temperatures it may be made of wrought iron, porcelain, or platinum, according to the

[1] Zeitschrift für physikalische Chemie **I**, 145.   [2] Journal für praktische Chemie **33**, 1.

intensity of the heat which it is desired to measure. The eudiometer B consists of a graduated tube which is open at the bottom and is provided with a stopcock at the top. It is surrounded by a glass water-jacket. By means of the stopcock at the bottom of the water-jacket and the tube which passes through the stopper at the top, water may be easily poured into or allowed to flow out of the outer glass cylinder. Gases which collect in the eudiometer may be rapidly put under atmospheric pressure and their volumes determined with great accuracy by means of this apparatus. A short piece of rubber tubing of small diameter and thick walls is used to connect the bulb A with the eudiometer B.

To determine the temperature of any substance with this instrument it is necessary to bring the level of the water on the outside and inside of the eudiometer to the zero point. Then if both A and B have acquired the temperature of the surrounding air they are connected by means of the rubber tubing. A definite volume of air under atmospheric pressure will now be contained in the bulb A and the tube which connects the bulb with the eudiometer. The temperature of the air confined in the apparatus is the same as that of the room in which the instrument is placed ;
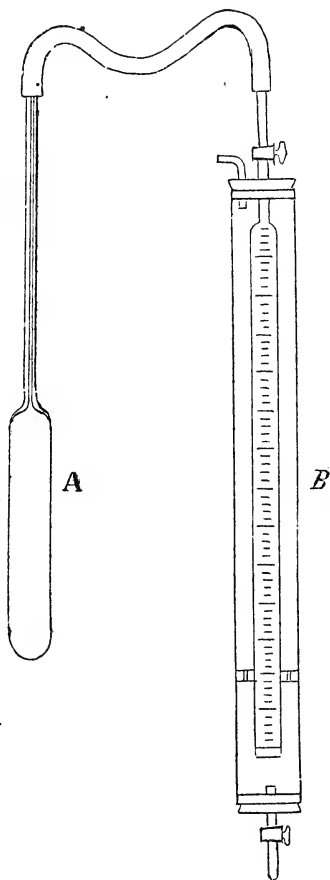
it is read off on a thermometer attached to *B*. The bulb *A* is then introduced into the heated substance. Air will be driven out of the bulb into the eudiometer. When the volume of gas in *B* no longer increases, water is allowed to flow out of the stopcock at the bottom of the water-jacket until the level of the liquid is the same on the outside and inside of the eudiometer. The volume of air in the eudiometer is then read off on the graduated tube.

The temperature to which the bulb has been raised may now be readily calculated by means of the formula

$$t' = t + \frac{V}{C - \dfrac{V}{273 + t}}$$

in which t' = the desired temperature expressed in degrees centigrade; t = the temperature of the room and eudiometer;[1] V = the volume of air measured in the eudiometer under atmospheric pressure, and C = a constant for any given temperature t. It depends upon the capacity of the bulb *A* and upon the coefficients of expansion of air, and of the material of the bulb at the temperature t.

The value of the quantity C may be easily determined by placing the bulb in steam, or any other vapor of known temperature, and measuring the volume of gas driven over into the eudiometer. Then by substituting the known quantities in the formula the equation may be solved for C.

The following temperature determinations were made with an apparatus the bulb of which had a capacity of about 60 cubic centimeters.

I.

Temperature of the room and pyrometer = 24°. In order to determine the value of C the bulb was plunged into steam. The volume of gas in the eudiometer (V) measured 9.6 cubic centimeters.

$$100 = 24 + \frac{9.6}{C - \dfrac{9.6}{297}},$$
$$C = .1586.$$

After the bulb had cooled down to the temperature of the room, and the level of the water in the eudiometer had been adjusted so

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[1] As only a very short time is required for a determination, the temperature of the eudiometer does not change appreciably. It is well, however, to protect the connecting tube and the eudiometer from the rays of heat by an asbestos or a wooden screen.

that it stood at the zero point, the air bulb was introduced into the vapor of boiling nitro-benzene.

Volume of gas expelled, $V = 18.2$ cc.

$$t = 24°,$$

$$t' = 24 + \frac{18.2}{.1586 - \frac{18.2}{297}} = 211°.$$

II.

Temperature of room and pyrometer $= 24°$. Volume of air expelled from the bulb by the vapor of boiling diphenylamine, $V = 22.7$ cc.; $t' = 300°$.

III.

Temperature of room and pyrometer $= 24°$. Volume of air expelled from the bulb by the vapor of boiling sulphur, $V = 27.5$ cc.; $t' = 440.7°$.

BRYN MAWR, PA., *May*, 1887.

XXVII.—BASIC LEAD NITRATES.

BY A. J. WAKEMAN AND H. L. WELLS.

The basic nitrates of lead have been investigated by a number of chemists. The existence of diplumbic nitrate, $Pb(NO_3)OH$, has been well established and frequently confirmed. In addition to this, a number of more basic salts have been described, but with quite discordant results, and some of these, made by precipitation with an alkali and not recrystallised, are open to doubt. The object of this investigation was to clear up the doubt concerning these more basic salts.

Berzelius obtained a salt to which he gave a composition corresponding to the formula $2(3PbO.N_2O_5).3H_2O$. The composition of this salt was afterwards confirmed by Meissner.[1] Volge[2] obtained a salt differing from that of Berzelius in containing double the number of water molecules. The most extended investigations of the subject, however, have been made by Löwe and Morawski. Löwe[3] describes two basic salts, the one a

[1] Jahresber. Fort. d. Chem. 1876, 194.   [2] Ann. d. Chem. u. Pharm. 94, 96.
[3] Jour. prakt. Chem. 1866, 388.

21

triplumbic nitrate having the formula $6PbO.2N_2O_5.2H_2O$, the other a salt having this formula less one molecule of water. Morawski[1] obtained a yet more basic salt to which he gave the formula $10PbO.3N_2O_5.5H_2O$. This and the second salt of Löwe were afterwards confirmed by Smolka.[2] The following is a summary of formulæ arrived at by the above named investigators:

Berzelius,	.	.	.	$6PbO.2N_2O_5.3H_2O.$
Meissner,	.	.	.	$\begin{cases} 6PbO.2N_2O_5.3H_2O. \\ 6PbO.2N_2O_5.H_2O. \end{cases}$
Volge,	.	.	.	$6PbO.2N_2O_5.6H_2O.$
Löwe,	.	.	.	$\begin{cases} 6PbO.2N_2O_5.2H_2O. \\ 6PbO.2N_2O_5.H_2O. \end{cases}$
Morawski,	.	.	.	$10PbO.3N_2O_5.5H_2O.$
Smolka,	.	.	.	$\begin{cases} 6PbO.2N_2O_5.H_2O. \\ 10PbO.3N_2O_5.5H_2O. \end{cases}$

From this table it is seen, therefore, that all the salts, with the exception of Morawski's and one of Smolka's, agree in the ratio of the lead oxide to the nitric acid, $3:1$, the difference occurring in the amount of water they contain. The method of analysis in some cases, however, as in that of Löwe, was questionable, the water being determined by drying, and the nitric acid by difference. In the present investigation, complete analyses have been made in every case, and, moreover, each product has been subjected to microscopic examination, and many which were mixtures were rejected. The salts were dried in each case over concentrated sulphuric acid, and special care was taken to avoid contact with carbonic acid.

The diplumbic nitrate was made in the first place, and the result of previous investigators was confirmed. This salt was found to possess a double crystalline form ; both flat scale-like crystals and prismatic crystals frequently separated from the same solution. The scaly crystals showed a mono- or triclinic habit, strong double refraction, brilliant polarisation colors, and an extinction angle of fourteen degrees. The prismatic crystals were too small and ill-defined to be studied with any degree of accuracy. No crystals were obtained sufficiently large for measurement. The following are results of analyses :

[1] Jour. prakt. Chem. 1830, 414.   [2] Monatsh. f. Chem. 1885, 195.

| | Scaly crystals. | | Mostly prismatic. | | | Calculated for Pb(NO₃)OH. |
	I.	II.	III.	IV.	V.	$Pb(NO_3)OH.$
PbO	77.39	77.41	77.04	76.69	78.37	77.96
N₂O₅	19.14	18.82	18.54	20.01	18.54	18.89
H₂O	3.51	3.68	3.56	3.20	3.27	3.15
	100.04	99.91	99.14	99.90	100.18	100.00

Repeated attempts were made to obtain the triplumbic nitrates, but in each case a single salt of different formula resulted. Following the directions given in Roscoe and Schorlemmer,[1] ammonia was added to a solution of normal lead nitrate in slight excess. A white powdery precipitate formed. The solution was boiled with addition of some of the normal nitrate until the odor of ammonia had nearly disappeared, and filtered while hot. A crystalline product separated from the filtrate while cooling. This was recrystallised. The crystals were flat tabular in shape, and of triclinic habit, with extinction angle of about thirty-five degrees. They showed an optical axis in convergent light, and gave a strong interference figure. They were too small, however, to be measured. The salt was found to be less soluble in water than the diplumbic nitrate. It was stable, undergoing no decomposition in boiling water nor by repeated crystallisation. The same salt resulted under varying conditions of concentration. The following are results of analyses of five separate samples of the salt, number II being the fourth recrystallisation of number I:

	I.	II.	III.	IV.	V.
PbO	84.82	84.79	84.75	84.95	83.66
N₂O₅	12.32	12.23	12.27	12.53	12.90
H₂O	2.61	2.81	2.64	2.65	2.94
	99.75	99.83	99.66	100.13	99.50

	Calculated for 10PbO.3N₂O₅.4H₂O.	Calculated for 3PbO.N₂O₅.H₂O. (Formula of Löwe and others.)
PbO	84.92	84.14
N₂O₅	12.34	13.60
H₂O	2.74	2.26
	100.00	100.00

Next, a large excess of ammonia was employed instead of a

[1] Vol. 2, Pt. I, p. 289.

slight excess as before, using different conditions of concentration
and length of time of digesting with ammonia. The resulting salt
crystallised in small crystals of triclinic habit resembling those
already described. The following results of analyses were ob-
tained on three separate products :

	I.	II.	III.
PbO	84.83	84.87	84.81
N_2O_5	12.10	12.43	12.17
H_2O	2.60	2.56	2.63
	99.53	99.86	99.61

These results agree closely with those just preceding, and show,
therefore, that the salts are identical.

When a very small amount of ammonia was employed, not an
excess, the resulting product was the diplumbic nitrate.

From these data, therefore, it may be safe to draw the conclusion
that, in the formation of basic lead nitrates by means of ammonia,
only one salt capable of recrystallisation results by the use of either
a slight or a large excess of the alkali.

In the examination of the salts resulting from the use of ammo-
nia, some difficulty was experienced from the fact that diplumbic
nitrate was frequently mixed with the more basic salt, as was
shown by microscopic examination ; such products were rejected.

Morawski[1] obtained a basic lead nitrate from his so-called
plumbonitratoglyceride by decomposing the same in boiling
water. This salt he calls a " pentaplumbic " nitrate, and gives to it
the formula $10PbO.3N_2O_5.5H_2O$, as before stated. This formula
differs from that of the salt just described only by a single water
molecule. Accordingly, Morawski's experiment was repeated
according to his directions, and the product recrystallised. An-
alyses of three consecutive crystallisations of the salt are as follows :

	I.	II.	III.
PbO	84.30	84.69	84.86
N_2O_5	12.34	12.93	12.11
H_2O	3.12	2.96	3.17
	99.76	100.58	100.14

This points clearly to the formula $10PbO.3N_2O_5.4H_2O$; showing,
therefore, that Morawski's salt is identical with the salt under

[1] Loc. cit.

consideration. It would seem, besides, from the average results of five analyses made by Morawski, that the formula $10PbO.3N_2O_5.4H_2O$ is indicated, rather than the one he assigned to the salt. Thus:

	Calculated for $10PbO.3N_2O_5.5H_2O$. (Morawski.)	Morawski's average of results.	Calculated for $10PbO.3N_2O_5.4H_2O$. (Wakeman and Wells.)
PbO	84.34	84.74	84.92
N_2O_5	12.25	11.88	12.34
H_2O	3.41	2.77	2.74
	100.00	99.39	100.00

Investigation was also made of Löwe's salt. He obtained his so-called triplumbic nitrate by precipitating in a basic lead acetate solution with potassium nitrate. He arrived at two formulæ: $3PbO.N_2O_5.H_2O$ and $2(3PbO.N_2O_5).H_2O$. The salt, made according to his method, was twice recrystallised, the crystals separating in little tufts, and resembling Morawski's salt in crystalline habit. Upon analysis they gave the following results:

	I.	II.
PbO	84.68	84.53
N_2O_5	12.41	12.41
H_2O	2.93	3.14
	100.02	100.08

To Löwe's salt, therefore, belongs the same formula,

$$10PbO.3N_2O_5.4H_2O.$$
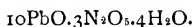
Thus the investigation of the basic nitrates of lead has resulted in the establishment of but a single recrystallisable salt besides the diplumbic nitrate.

The method devised by one of us[1] for the analysis of basic cupric nitrates has been employed in the analyses given in this article.

Our thanks are due to Mr. S. L. Penfield, who has given us much advice and assistance in the microscopic examination of our products.

[1] Wells and Penfield, Amer. Jour. of Science [III] **30**, 50.

XXVIII.—BASIC ZINC AND CADMIUM NITRATES.

By Horace L. Wells.

Klinger[1] has described a basic cadmium nitrate to which he gives the formula $Cd{<}^{NO_3}_{OH}.H_2O$. He made this salt, together with basic lead nitrate, by adding lead hydroxide to a hot cadmium nitrate solution, filtering and cooling; also by heating normal cadmium nitrate, and, more easily, by dissolving cadmium hydroxide in hot cadmium nitrate solution, when the salt crystallised out on cooling. His salt was freed from normal nitrate by washing with alcohol.

I have confirmed Klinger's result[2] as follows: Cadmium oxide was added to a hot concentrated solution of normal cadmium nitrate as long as it continued to dissolve, the liquid was filtered hot, and, upon cooling, a good crop of very thin scaly crystals separated; they were collected on a filter, washed thoroughly with absolute alcohol and dried over sulphuric acid. When dry they had a pure white color and possessed a beautiful pearly lustre, as is usual with very thin crystals. Analysis gave the following results:

	Found.	Calculated for $N_2O_5.2CdO.3H_2O$.
N_2O_5	26.01	25.83
CdO	60.99	61.25
H_2O	13.08	12.92
	100.08	100.00

Since no zinc nitrate has been described corresponding to this cadmium salt, and since, as far as I know, indeed, none has been made which has been washed with alcohol to avoid decomposition with water, a basic zinc nitrate was made in exactly the same manner as the cadmium salt, by the use of concentrated zinc nitrate solution and zinc oxide. It was carefully washed with absolute alcohol and dried over sulphuric acid. The salt was obtained in

[1] Berichte d. deutsch. chem. Gesell. **16**, 997.

[2] The figures given in Klinger's article do not agree with his formula; he gives:

	"Gefunden.	Berechnet.
CdO,	61.28, 61.11	61.17
H_2O,	8.52	8.63."

These figures would give the formula $4N_2O_5.7CdO.7H_2O$ instead of $N_2O_5.2CdO.3H_2O$. Since my results agree with his formula, I conclude that there is a mistake in his published figures.

very slender prismatic crystals, entirely different in appearance from the cadmium compound. When dry it appeared and felt much like a mass of cotton. It was analysed with the following results:

	Found.	Calculated for $N_2O_5.2ZnO.3H_2O$.
N_2O_5	33.43	33.33
ZnO	50.07	50.00
H_2O	17.16	16.67
	100.66	100.00

Thus it is seen that the basic nitrates of zinc and cadmium, as might be expected, correspond exactly in composition.

These two salts are very readily decomposed by water; even ordinary strong alcohol decomposes them slowly. A sample of the cadmium salt washed once with cold water with a suction pump gave on analysis:

		Ratio.
N_2O_5	22.93	1.
CdO	64.34	2.38
H_2O	12.93	3.38
	100.24	

The fact that some normal nitrate probably remained in this product shows how readily it is decomposed by water.

Several samples of both salts were made and washed with water under varying conditions, in order to study the decomposition and to decide if any definite basic nitrate could be thus made.

The following are analyses of separate samples washed with cold water with a suction pump not much more than enough to remove the normal nitrate. They were all dried over sulphuric acid.

From zinc salt:

	A.			*B.*	
		Ratio.			Ratio.
N_2O_5	17.42	1.		15.00	1.
ZnO	65.11	5.		67.09	5.94
H_2O	17.45	6.		17.75	7.10
	99.98			99.84	

From cadmium salt :

	A.		B.		C.	
		Ratio.		Ratio.		Ratio.
N₂O₅	12.35	1.	12.38	1.	11.75	1.
CdO	74.34	5.06	74.81	5.09	75.36	5.40
H₂O	13.46	6.50	12.88	6.22	12.77	6.50
	100.20		100.07		99.88	

The following were washed excessively with *cold* water and dried over sulphuric acid.

From zinc salt :

		Ratio.
N₂O₅	15.45	1.
ZnO	66.43	5.73
H₂O	18.01	6.22
	99.89	

From cadmium salt :

		Ratio.
N₂O₅	7.53	1.
CdO	79.36	9.
H₂O	12.51	10.
	99.40	

The following were thoroughly washed with *hot* water and dried over sulphuric acid.

From zinc salt :

		Ratio.
N₂O₅	0.20	...
ZnO	97.40	10.
H₂O	2.22	1.
	99.81	

From cadmium salt :

		Ratio.
N₂O₅	0.30	...
CdO	86.60	1.
H₂O	12.16	1.
	99.06	

It appears from the above results that the cadmium salt is decomposed to a greater extent by cold water than the zinc salt. It seems also that, after a certain amount of decomposition has

taken place, further change, particularly in the case of the zinc salt, takes place very slowly, if at all ; this indicates the possibility of the existence of more basic nitrates, perhaps $N_4O_5.5ZnO.6H_2O$ or $N_2O_5.6ZnO.7H_2O$, and the corresponding cadmium compounds. It is to be noticed, however, that if the ratio $N_2O_5 : ZnO$ or $CdO : H_2O = 1 : 2 : 3$ be subtracted from the ratios found for the products washed with cold water, the remainder is always close to ZnO or $CdO : H_2O = 1 : 1$; hence all these products may be regarded as mixtures of the $1 : 2 : 3$ nitrates with different amounts of the hydroxides. Even if it is necessary to assume that more basic nitrates exist, it would be difficult to decide upon their composition, since the products are wholly amorphous, and there is no means for deciding how much hydroxide is mixed with them, or whether they do not contain more than one basic nitrate.

It is an interesting fact, brought out by the last two analyses, that by washing with hot water the cadmium salt leaves the hydroxide, while the zinc salt leaves the almost pure oxide as a residue.

Previous investigators of basic zinc or cadmium nitrates, with the exception of Klinger, whose work is referred to at the beginning of this article, have apparently washed their products with water, or experimented in a still more uncertain way by heating the normal nitrate and analysing the residue which happened to be left. The following is a summary of the previous results as far as I have been able to find them. The formulæ have been transformed for the sake of easy comparison, and have been translated into the new system when necessary.

Grouvelle[1] was the first investigator of basic zinc nitrates. He formed it by heating the normal nitrate, $N_2O_5.8ZnO.2H_2O$, and by adding a small quantity of ammonia to a solution of the normal nitrate, $N_2O_5.8ZnO.4H_2O$.

Schindler[2] made $N_2O_5.8ZnO.2H_2O$ in the same way as Grouvelle, thus confirming the latter's result ; he made also $N_2O_5.4ZnO.2H_2O$ by boiling the first compound with solution of the normal nitrate.

Ordway[3] analysed the mass left by heating normal zinc nitrate and obtained $N_2O_5.4ZnO.3H_2O$.

[1] Ann. de Chim. et de Phys. 1821 [2] **19**, 137.

[2] Gmelin's Handbook, London Ed. **5**, 34 ; Würtz Dict. de Chim. ; Watts' Dictionary. Reference to original article could not be found.

[3] Am. Jour. Sci. [2] **32**, 14.

Gerhardt[1] also made $N_2O_5.4ZnO.3H_2O$, in prismatic needles.   I have been unable to consult his original article[2] and do not know how this was prepared.

Bertels[3] showed that the vitreous mass obtained by Ordway has not a constant composition, but by treating this mass with water he obtained $4N_2O_5.7ZnO.14H_2O$.   This is quite close to my formula, $N_2O_5.2ZnO.3H_2O$; he could not have washed this much with water.   Bertels obtained also $N_2O_5.6ZnO.8H_2O$ by treating an excess of metallic zinc with nitric acid.

Habermann[4] made $N_2O_5.5ZnO.5\frac{1}{2}H_2O$ by treating normal zinc nitrate solution with ammonia as long as a precipitate formed, and washing the product with water ; in the same manner he obtained from cadmium nitrate solution $N_2O_5.12CdO.11H_2O$.

It seems probable that all the above compounds, except Ordway's and the first of Bertels, are decomposition products made by washing the $1:2:3$ basic nitrate with water.   The fact that several of them have less water than I have found in such products can be explained if it is supposed that they were dried at $100°$; for I have found that the zinc product which gave a ratio $1:5:6$ (A above) slowly lost a weight corresponding to about one-half of its water when so heated.

In conclusion it may be suggested that all basic nitrates of zinc and cadmium, except the $1:2:3$ salts, be rejected until, by more positive evidence, their existence is established.

[1] Jahresbericht, 1847-8, 436.   [2] J. Pharm. [3] **12**, 61.
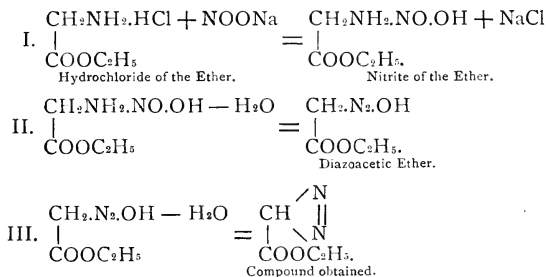[3] Jahresbericht, 1874, 271.   [4] Monatsh. fur Chem. 1884, **5**, 447.

NOTES.

The Discovery of Diamide or Hydrazine.

In the course of an investigation on glycine, $CH_2 \begin{cases} NH_2 \\ COOH \end{cases}$, Theodore Curtius found in 1883[1] that by the action of sodium nitrite on the hydrochloride of the ethyl ether of glycine a diazo-compound, $CH.N_2.COOC_2H_5$, is formed. The following formulas illustrate the formation of this compound:

I.
$$\begin{array}{l} CH_2NH_2.HCl + NOONa \\ | \\ COOC_2H_5 \\ \text{Hydrochloride of the Ether.} \end{array} = \begin{array}{l} CH_2NH_2.NO.OH + NaCl \\ | \\ COOC_2H_5. \\ \text{Nitrite of the Ether.} \end{array}$$

II.
$$\begin{array}{l} CH_2NH_2.NO.OH - H_2O \\ | \\ COOC_2H_5 \end{array} = \begin{array}{l} CH_2.N_2.OH \\ | \\ COOC_2H_5. \\ \text{Diazoacetic Ether.} \end{array}$$

III.
$$\begin{array}{l} CH_2.N_2.OH - H_2O \\ | \\ COOC_2H_5 \end{array} = \begin{array}{l} CH \diagdown \begin{array}{l} N \\ || \\ N \end{array} \\ | \\ COOC_2H_5. \\ \text{Compound obtained.} \end{array}$$

Further investigations have shown that this compound is in all probability a diazoacetic ether, that is, acetic ether in which two hydrogen atoms of the methyl group are substituted by a double atom of trivalent nitrogen ($-N = N -$).

In order to test his hypothesis, Curtius prepared the nitrite of the ethyl ether of glycine, and obtained directly from it the diazo-acetic ether by loss of two molecules of water.[2]

The difference between the constitution of the diazoacetic ether and the hypothetical diazobenzene is expressed by the following formulas:

I.
$$\begin{array}{l} CH \diagdown \begin{array}{l} N \\ || \\ N \end{array} \\ | \\ COOC_2H_5. \\ \text{Diazoacetic Ether.} \end{array}$$

II.
$$\begin{array}{l} CH_2 - N = N - OH \\ | \\ COOC_2H_5. \\ \text{Hypothetical Diazoacetic Ether (analogous to the hypothetical diazobenzene.)} \end{array}$$
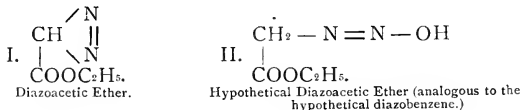
In I the two free affinities of the double atom of nitrogen saturate two affinities of the methyl carbon of the acetic acid; in II only one, while the other free affinity is saturated by a hydroxyl. It

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[1] Berichte d. deutsch. chem. Gesell. **16**, 754, 2230.   [2] Ibid. **17**, 953.

is possible that the remarkable stability of the diazo compounds of the ethers of the fatty series is due to this closer connection of both nitrogen atoms with the carbon of the methyl group of the acetic ether. This stability is so great that the diazoacetic ether can be distilled at ordinary pressure without undergoing decomposition. Diazoacetic ethyl ether has the constant boiling point $143°$ (barometric pressure $= 721$ mm.).

It seemed at first probable that diazo compounds of the fatty acids can only exist if the hydroxyl in the carboxyl group is replaced by an alkyl. Curtius, however, has shown that the amido group can substitute efficiently the alkyl. Treating diazoacetic ether with ammonia in watery solution he obtained a compound which he calls diazoacetamid, and to which he gives the

$$\text{formula } \underset{\underset{\text{CONH}_2}{|}}{\text{CH}} \overset{\diagup \text{N}}{\underset{\diagdown \text{N}}{\|}}$$
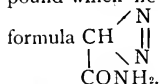
Within a few weeks past Curtius has obtained[1] the potassium salt of a new diazo fatty acid by treating diazoacetic ether with hot concentrated caustic potash. He says nothing about the constitution of the new acid, except that it is closely related to the derivatives of pseudo-diazoacetamid. If the golden yellow solution of this new acid is digested for a short time with very dilute sulphuric acid, it loses its color without evolution of nitrogen, and on cooling, colorless, beautiful crystals appear. This substance is the sulphate of the long sought diamide or hydrazine $\underset{\underset{\text{NH}_2}{|}}{\text{NH}_2}$

The free diamide can be obtained by heating its salts with solutions of alkali. It is a gas of great stability, which dissolves very easily in water and turns red litmus paper blue. In a concentrated state it possesses a very peculiar odor which is but little suggestive of ammonia.

Hydrazine possesses strong reducing properties. Its chemical behavior corresponds to that of the substituted hydrazines.

E. A. S.

[1] Berichte d. deutsch. chem. Gesell. **20**, 1632.

AMERICAN

CHEMICAL JOURNAL.

IV.—NOTES ON THE SODA-LIME METHOD FOR DETERMINING NITROGEN.

By W. O. Atwater and C. D. Woods.

A series of studies of the chemistry of animal tissues, especially of fish, in this laboratory, have involved a large number of nitrogen determinations for which the soda-lime method had been employed. The importance of securing results as nearly accurate as practicable has led to a number of observations regarding the methods of manipulation and the sources of error and ways of avoiding them. The accuracy of the soda-lime method has been called in question, and there are still wide divergences of opinion regarding some of the details, despite the pains that have been taken to investigate them. Partly because our experience has convinced us that when rightly manipulated it gives excellent results, and partly because of the propriety of describing the methods followed in the studies referred to, in connection with an account of them to appear in these pages, the following statements seem not out of place. We shall speak first of some points regarding reagents, apparatus, and manipulation.

23

Soda-lime.

Preparation.—Instead of buying soda-lime at the ordinary price,
we have found it very easy and far more economical to make it in
the following way, which we believe is practised elsewhere :

One kilogram of commercial caustic soda is dissolved in hot
water and the solution poured upon 2.5 kilos of pulverised quick-
lime in an iron kettle, care being taken to have enough water in
the solution to ensure the slaking of the lime. The kettle is put
over a hot fire and the contents are well stirred until the excess of
water is removed and the mass is fused. It is ground while warm
and kept in tightly stoppered bottles (caoutchouc stoppers have
not, in our experience, sufficed to keep out the moisture on long
standing) until used. Enough for several hundred nitrogen deter-
minations is thus easily made in a very short time and at a cost for
materials scarcely worth mentioning.

The use of an iron or Hessian crucible, as commonly recom-
mended,[1] for fusing the soda-lime we find entirely unnecessary.
The precaution that the soda-lime should not contain enough of
carbonates to effervesce strongly on application of acid[1] is, of
course, needless when this way of making is followed, and would
seem, from the results obtained with Johnson's soda-lime (see
beyond), to be entirely uncalled for.[1]

We have found it convenient to divide the ground material into
a finer portion with which the substance containing the nitrogen to
be determined is mixed, and a coarser portion to be used for the
anterior layer in charging the combustion tubes. That which
passes through a sieve with meshes of $\frac{3}{4}$ mm. works very well
for the finer, and that which, not passing this sieve, passes one
of 2 mm. is satisfactory for the coarser portion. An ordinary
drug mill, which costs but little and is useful for other purposes,
serves well for the grinding.

Effect of varying proportions of soda and lime.—The follow-
ing figures from our laboratory note-books are perhaps worth
recording. The determinations were made with specimens of soda-
lime in which 1.75, 2, and 2.5 parts by weight of quick-lime were
used for each part of caustic soda. The mixtures are computed
to contain from 22 to 16 per cent. of sodium oxide. The percent-
ages of nitrogen are calculated on water-free substance.

[1] Vid. Neues Handwörterbuch der Chemie 1, 482, and Fresenius' Quant. Analysis.

TABLE I.

In Flesh of	Percentages of Nitrogen obtained.	
	Soda : lime :: 1 : 1.75	Soda : lime :: 1 : 2
Lobster, . . .	13.10	13.09
Mullet, ...	12.44	12.47
Yellow Perch, .	14.52	14.55
Sheep, ...	6.97	6.96
"	3.58	3.59
	Soda : lime :: 1 : 1.75	Soda : lime :: 1 : 2.5
Sheep, ...	5.56	5.59
"	5.98	6.02
"	7.36	7.38
"	4.67	4.71
"	4.65	4.62

The above determinations, which, it will be observed, were made in flesh with varying quantities of fat, from that of fish containing only a fraction of one per cent. to that of sheep (mutton) in which the fat very largely exceeds the protein, show no disagreement of duplicates exceeding 0.04 per cent., and imply that the quantity of nitrogen obtained is the same whether the larger or the smaller proportion of lime is used. The soda-lime with $1\frac{3}{4}$ part of lime to one of soda was very fusible. That with $2\frac{1}{2}$ of lime to one of soda was reasonably hard, and was used in nearly all of the determinations hereafter reported. For a time we were inclined to like the more fusible mixture, since in the combustion it distributed itself over the inner surface of the tube, leaving in the anterior portion a channel, through which the gases formed in the combustion must pass. For reasons to be given later, it is our belief that one source of error in the soda-lime method is the incomplete ammonification of the nitrogenous compounds formed by the destructive distillation, and that to obviate this difficulty it is well for the gases to pass over a large surface of hot soda-lime. The formation of this tubular channel in the anterior portion of the combustion tube seemed especially favorable for bringing the gases into contact with the soda-lime, but the very fusible soda-lime is in some respects inconvenient, and after a time we came back to the use of the comparatively infusible mixture of one part of caustic soda to $2\frac{1}{2}$

of lime, depending upon the coarse particles in the anterior layer of soda-lime for the needed surface.

Ordinary vs. Johnson's soda-lime.—The mixture of sodium carbonate and slaked lime recommended by Johnson[1] has proved very satisfactory, being easily and cheaply made, and, so far as we have observed, giving the same results as the common soda-lime, as shown in Table II.

TABLE II.

In Flesh of	Percentages of Nitrogen found with	
	Ordinary Soda-lime.	Johnson's Soda-lime.
Halibut, ...	6.03	6.04
Herring, . . .	7.04	7.01
Salmon, ...	8.76	8.75
"	9.89	9.84
Shad, ...	9.92	9.87
Porgy, ...	10.78	10.75
Mackerel, . . .	11.26	11.23
Trout, ...	13.25	13.24
Flounder, . . .	14.11	14.09

The figures obtained with the two kinds of soda-lime are practically identical, thus agreeing with those obtained by Johnson and Jenkins.[2]

We might add that in determinations of nitrogen in vegetable material (peas) by Mr. Haynes, a student in this laboratory, slaked lime as recommended by Johnson[3] gave the same results as soda-lime. These and other observations, which it will perhaps be superfluous to cite in detail, seem to imply that neither the presence of carbonic acid in the soda-lime nor the proportions of lime and soda, at least within the limits which obtained in the above cases, have any appreciable effect upon the amount of nitrogen obtained from the nitrogenous compounds of flesh. The practical identity of the results obtained with these different reagents accords entirely with the idea which has been brought prominently forward of late, that the ammonifying agent is superheated steam.[4]

Testing the purity of soda-lime by sugar and other reagents.—In testing the purity of soda-lime by combustion with sugar, as

[1] This Journal **1,** 77. [2] Loc. cit. [3] This Journal **6,** 61.
[4] Vid. Grouven, Landw. Vers. Stationen **28,** 343, and Johnson, loc. cit.

is sometimes recommended, we have occasionally met with very perplexing results. At times we have found apparent indications of nitrogen, while at other times, with the same materials, more alkali was required to neutralise the acid after than before the combustion, which implied that acid products had been formed from the sugar. To obtain some definite data on this matter the determinations in Table III were made. To insure correctness in measurements of the standard solutions, extremely narrow burettes, graduated to fiftieths of a cc., were employed, and especial pains were taken, by cleaning the burettes and working at ordinary temperature, to make the titrations accurate.[1] One cc. of standard acid was used in each case. The quantities of solution to be titrated were thus so small that with cochineal solution very accurate titration was possible. The sugar employed was that commonly sold in large crystals as " rock candy," and was recrystallised from alcohol to insure greater purity. One cc. of standard acid corresponded to, approximately, 10 mgm. of nitrogen. At each titration of acid used for the combustion a cubic centimeter of fresh acid was compared with the alkali. The results of the two titrations are placed opposite each other in the table. Tests made at the same time with oxalic acid and stearin are given with those of the sugar. By medium heat is to be understood a temperature high enough to make the combustion tube slightly red and give a tinge of the familiar yellow color to the soda-lime ; by high heat, a heat as great as the tubes, of the most difficultly fusible Bohemian glass we could obtain, would endure without bursting, the quantity of acid in the bulb tube being made very small so as to reduce the pressure to a minimum. The agreement of titrations in the combustions of stearin and oxalic acid implied that the latter, as well as the soda-lime, were free from nitrogen and yielded no acid products. The differences in the amounts of standard alkali required for neutralisation after the combustions with sugar, though absolutely small, were evidently much outside the limits of error, and are most easily explained by the assumption that the sugar contained a minute trace of nitrogen, which appeared as ammonia in the first of the two cases where the combustion was carried on at medium heat, and was more than neutralised by the acid products formed at high heat. The difference between the results with sugar at medium heat and those with

[1] See article on " Burettes and Pipettes " in Journal of Analytical Chemistry, Vol. 1, Part 4.

stearin and oxalic acid was about o.12 cc. of alkali, which would be equivalent to some o.3 mgm. of nitrogen. This would imply o.07 per cent. of nitrogen in the sugar. The determinations at high heat implied an amount of acid distilled over enough to neutralise this amount of ammonia, and that about as much more should be formed in the destructive distillation of sugar is what would be naturally expected when we consider what are the usual products of distillation of materials poor in nitrogen, such as wood.[1]

Table III.

Combustion of Stearin, Oxalic Acid, and Sugar with Soda-lime.

Substance.		Time of Combus-tion.	Heat of Combustion.	Standard Alkali Solution re-quired to neutralise 1 cc. of Standard Acid.	
Kind.	Weight.			In Standard-ising.	After Combustion.
	Grams.	Minutes.		cc.	cc.
Stearin, . . .	0.433	115	Medium.	4.34	4.34
" . . .	0.442	70	High.	4.33	4.34
Oxalic Acid, . .	0.408	76	Medium.	4.32	4.33
" . .	0.410	52	High.	4.32	4.33
Sugar, ...	0.401	65	Medium.	4.33	4.23
"	0.399	93	"	4.33	4.19
"	0.487	45	High.	4.31	4.44
"	0.401	45	"	4.31	4.41
"	0.412	45	"	4.33	4.42

Assuming this explanation to be correct, the amounts of nitrogen and acid products are both too small to be of great consequence. The results of these determinations, however, seem to us to help toward an explanation of some of the discrepancies so often observed in the results obtained from the use of sugar in com-bustions, and to indicate that stearin or oxalic acid is to be preferred for testing the purity of soda-lime.

Apparatus and Manipulation.

Nitrogen bulbs.—For the Knop and Arendt nitrogen bulbs, which, after no little experience with numerous kinds of bulbs and U-tubes, we have, in common with many other chemists, found most satisfactory, we find a slight modification of the ordinary

[1] See accounts of decomposition of sugar by other agencies, and formation of acid products, *e. g.* Conrad and Guthzeit, Ber. deutsch. chem. Ges. 1885, **1,** 439.

form decidedly preferable. This consists in a small bulb of the shape of an ordinary thistle-tube bulb, but of only about 6 or 7 mm. diameter at the outer end in the place of the ordinary point.[1] The great advantage of this is that the acid can be drawn into it directly from the burette, while it offers no impediment to rinsing out completely.

Rinsing the nitrogen bulbs with ordinary distilled water.—Since the distilled water of the laboratory commonly contains small quantities of ammonia, a minute but appreciable error may be introduced when this is employed for rinsing the bulbs before titrating. This error may be made inappreciable by using very small quantities of the water for rinsing. We have found 10 cc. of water sufficient to rinse our Knop and Arendt bulbs, so that no trace of acid or ammonia could be found by further rinsing.

The following results of a test to determine how large the error would be from using a sample of distilled water from the tank in our laboratory, though made simply for our own satisfaction and of no great importance, will perhaps be worth the space they take in print. In each trial one cc. of standard acid was drawn into the nitrogen bulb and poured out again. The bulb was thereafter rinsed in successive trials with varying amounts of the distilled water. When the smaller quantities of the latter were used, water freed from ammonia by redistillation with potassium hydroxide and permanganate, and rejection of so much of distillate as gave a visible reaction with Nessler's reagent, was added to make the volume alike in all. Using the very narrow burettes for measuring and cochineal as an indicator, as was done in the previous experiments, the figures of Table IV were obtained, those for each series representing the averages of practically identical, duplicate results.

TABLE IV.

Number of Trials.	Standard Acid used.	Distilled Water added.	Pure Water added.	Total Solution.	Alkali required to neutralise.
3	1 cc.	10 cc.	90 cc.	101 cc.	4.33 cc.
2	1 "	50 "	50 "	101 "	4.30 "
2	1 "	100 "	none.	101 "	4.26 "

[1] I have an impression that this idea is a German one, but do not recall any description of it, except in catalogues of manufacturers who have made the apparatus in this form in accordance with directions from here.—W. O. A.

As 1 cc. of the standard acid was equivalent to 10 mgm. nearly of nitrogen, the extreme difference, (4.33—4.26) 0.07 cc. of standard alkali, corresponding to the ammonia introduced with 90 cc. of distilled water, would be equivalent to a trifle less than 0.2 mgm. of nitrogen. Unless, therefore, the ammonia in the distilled water should be very much more than in the specimen here used, to heed it in ordinary work would be simply hair-splitting. But where the greatest possible accuracy is required it would seem desirable to at least test the water used, or to use very little. Ordinary well or reservoir water would often be preferable to distilled water for rinsing.

Burettes. Standard acid and alkali solutions. Indicator.—A small quantity of acid in the nitrogen bulb offers less resistance to the passage of the gases, and hence causes less tension inside the combustion tube to expand the latter, than a larger quantity. The smaller the amount of liquid to be titrated the sharper is the reaction. For both these reasons, concentrated solutions seem to us desirable. The great accuracy as well as convenience of very narrow burettes has led us to discard those of ordinary width and to use very narrow ones. For standard acid, a 10 cc. burette graduated to twentieths of a cc., the length from the 0 to 10 mark being about 40 cm., has proved very satisfactory. For the alkali, which may be more dilute than the acid, a somewhat wider burette is convenient. A standard acid of which 10 cc. corresponds to 100 mgm. of nitrogen we find very convenient. If ammonia is used for the alkali, we believe the solution should be titrated against the acid each day it is used, although we have found our standard ammonia solutions to change but very little from month to month.

For an indicator of the neutral point we prefer cochineal to litmus. Besides its commonly urged advantage of being so little affected by carbonic acid, we find that with freshly prepared cochineal solution the change in color from acid to alkaline is very quick and sharp and that the color is more permanent, so that there is less liability to error if the neutralisation is not completed at once. A solution prepared by boiling two grams of commercial cochineal with 100 cc. of water and adding alcohol has proved very satisfactory in our experience. Two drops of this are sufficient to color 100–200 cc. of an acid or alkaline solution.

Length of combustion tubes and method of charging.—As these details have been subjects of no little discussion in connection with the question of the sources of error in the soda-lime method, we give the results of comparative tests made in the course of a series of analyses of flesh of fish. Perhaps the best way to explain the charging of the tube will be by the accompanying tabular statement, in which the figures represent approximate lengths, and are those gradually settled upon after numerous trials with tubes of different lengths and charged in different ways. We intend to have at least forty parts by weight of fine soda-lime for every part of substance in the "mixture." About 0.4–0.6 gram of flesh (water-free), or more in case it contains much fat, we find convenient quantities. Especial stress is laid upon the importance of having the tube so filled with the soda-lime as to leave no considerable open space. The channel, commonly recommended for free passage of the gases, may cause serious error, as will be shown later.

Length of tube,	40 cm.
Asbestos and fine soda-lime, ·	4 "
Mixture, fine soda-lime and substance,	16 "
Rinsings, fine soda-lime,	4 "
Anterior layer, coarse soda-lime,	12 "
Asbestos, open space, plug,	4 "

A number of comparative trials with larger quantities of soda-lime mixed with the substance to be analysed, sufficient to make the mixture fill about 26 cm. of the tube, gave results practically identical with those obtained when the tubes were charged as here stated.

In the comparative tests with longer anterior layers of soda-lime and correspondingly longer tubes, the charging of the tubes was as just explained, except that while in the ordinary 40 cm. tubes the anterior layer was about 12 cm. long, in the 60 cm. tubes it was approximately 32 cm., and in the 75 cm. tubes nearly 50 cm. The figures of Table V will suffice to show the outcome of a much larger number of trials which they fairly represent. In the cases indicated by the * the "high heat," and in the others the "usual" or "medium heat" (see description of Table III above), was used.

Table V.

*Comparison of amounts of Nitrogen obtained with longer and
shorter combustion tubes.*

In Flesh of	Percentages of Nitrogen obtained with tubes of		
	40 cm.	60 cm.	75 cm.
Red Snapper, . . .	...	14.84*	14.80*
Haddock, ...	14.75*	14.76*	14.81*
Flounder, ...	14.13*	14.17*	14.09*
Mackerel, ...	5.82	5.88	
Spanish Mackerel, .	10.75	10.77	
White Perch, . . .	11.82	11.76	
Mascalonge, . . .	13.79	13.85	
White Perch, . . .	13.40	13.44	
Herring, ...	10.19	10.24	
Sheepshead, . . .	11.89	11.91	
Turbot, ...	8.24	8.26	
Pike Perch, . . .	14.66	14.67	
Black Bass, . . .	14.86	14.84	
Lobster, ...	11.85	11.85	
Scallops, ...	10.83	10.85	
Oysters, ...	8.48	8.44	
"	8.84	8.79	
"	7.10	7.05	
"	8.31	8.33	
"	7.85	7.83	
"	9.26	9.22	
"	8.38	8.39	
"	7.15	7.15	

* High heat.

These figures seem to us sufficient to show that in flesh of fish
and oysters, at any rate, the difference of 20 cm. or more in the
length of the combustion tube, *i. e.* in the length of the anterior
layer of soda-lime, does not make any appreciable difference in the
amount of nitrogen obtained, provided the above-mentioned pre-
cautions are observed and enough of soda-lime is well mixed with
the substance, and a moderately long anterior layer of soda-lime,
12–20 cm., is provided. Similar experience with other kinds of
animal and vegetable materials, the results of which are scattered
through our laboratory note-books, has left us with the very
decided impression the same is true of animal and vegetable tissues
generally, except in cases to be mentioned hereafter, in which

volatile nitrogenous distillation products are formed and escape ammonification unless unusual precautions are taken. We have often used shorter tubes, from 30 to 35 cm., and have not observed any difference in results, but feel safer with tubes of from 36 to 40 cm. length for ordinary work. But, as will be insisted later, we are persuaded that careful mixing of substance with soda-lime, close packing of the tube, and careful heating, so as to insure complete decomposition of the substance and sufficient contact between distillation products and hot soda-lime, and not too slow conduct of the combustion, are important, otherwise there is danger of loss of nitrogen.

Comparison of Soda-lime and Absolute Methods.

Further observations upon the soda-lime method will be given in succeeding papers. Meanwhile we may here cite some tests of the accuracy of the work by the method just explained, which were made by comparison with the volumetric method. Previous to the making of the volumetric analyses, however, we felt that the method itself needed some examination, not only on account of the need of preliminary practice as a general principle, but because of the sources of error to which determinations are unavoidably exposed. The details of the work were carried out by Dr. J. H. Long, then assistant in this laboratory, and since Professor of Chemistry in Northwestern University and the Chicago Medical College.

The apparatus used and method followed were very similar to those described by Johnson and Jenkins.[1] A few deviations from the method were made, however, of which one was the omission of the potassium chlorate in finishing the combustion. Some minor corrections were also introduced, as detailed beyond. Common experience shows that the absolute method is apt to give rather high percentages of nitrogen. Where the mercury air-pump is depended upon to exhaust the combustion tube, a larger or smaller error in this direction may occur from the incomplete pumping out of the air before the combustion. Various means have been suggested to avoid this. It is sometimes recommended to continue the pumping until the "click" of the mercury in the pump is heard. We have found this hardly sufficient for the most accurate work, and prefer to pump half an hour or so longer, both

before and after the combustion. Even after this a not inconsiderable amount of air remains in the interior of the combustion tube adhering to the glass and contents. A determination in how far an ordinary combustion, such as we were in the habit of making, would be affected by this residual air was attempted by blank combustions in which oxalic acid, previously found to yield no nitrogen (as ammonia) to soda-lime, was employed. Four determinations gave respectively 0.3 cc., 0.6 cc., 0.5 cc. and 0.6 cc. of gas (nitrogen), or on the average 0.5 cc. This quantity was deducted from the volume found in each of the volumetric determinations of nitrogen which follow.

When the nitrogen is collected over potassium hydroxide solution, the vapor tension of the latter may, unless the solution is concentrated, introduce a slight error in the measurement of the gas, as has been observed by Schiff.[1]

Even a 50 per cent. KOH solution gives an appreciable vapor tension, as has been shown by Wüllner.[2] Wüllner's statements are not perfectly clear at first reading, but the facts appear from his formula for the tension, $V = 0.003320\,T - 0.00000432\,T^2$, where V is the decrease of tension for every part of " pentahydrate of potash " to 100 of water (which we understand to be equivalent to $0.51 K_2O : 100 H_2O$, or 0.51 gram K_2O in 100.51 grams of potassium hydroxide solution).

Dr. Long has made several determinations of the vapor tension of a potassium hydroxide solution of sp. gr. 1.36, using a kathetometer and eudiometer for the purpose. He finds:

Vapor Tension of Potassium Hydroxide Solution of Sp. Gr. 1.36.

At temperature, C.,	6.2	7.1	9.5	14.5
Vapor tension,	2.6 mm.	3.0 mm.	4.0 mm.	6.5 mm.

These results Dr. Long computes to be in accordance with Wüllner's formula. The correction for vapor tension is a small one, but is yet an appreciable quantity.

In the following determinations of nitrogen by the absolute method the charging of the tubes was as indicated below. The total length of the tube was about 80 cm.

CuO. 5 cm.	Fine CuO and substance. 25 cm.	Coarse CuO. 10 cm.	Copper gauze. 10 cm.	Coarse CuO. 10 cm.	$HNaCO_3$, asbestos and stopper about 15–20 cm.

[1] Zeitsch. f. Anal. Chem. **7**, 432.   See also Kreussler, Landw. Vs. St. **31**, 236.
[2] Pogg. Annalen **110**, 1860, 570.

Corrections for residual air (nitrogen) in the combustion tube and for vapor tension of sodium hydroxide solution were made as above described; the latter correction, however, is applied separately to the percentages of nitrogen in Tables VI and VII herewith, to show more plainly its effect on the result. It is superfluous to add that the nitrogen was measured in a calibrated eudiometer and that the corrections for temperature and barometric pressure were made in the ordinary manner.

TABLE VI.

Nitrogen in Pure Ammonium Oxalate.

	A.	B.	C.
Ammonium oxalate taken	0.5000 grm.	0.6000 grm.	0.6000 grm.
Volume of N found,	79.2 cc.	94.6 cc.	94.4 cc.
Weight of N found,	0.0995 grm.	0.1189 grm.	0.1186 grm.
Per cent. of N found,[1]	19.90 per ct.	19.82 per ct.	19.77 per ct.
Per cent. of N corrected,[2]	19.84 "	19.75 "	19.71 "

TABLE VII.

Nitrogen in Pure Ammonium Sulphate.

	A.	B.	C.	D.
Ammonium sulphate taken,	0.6000 gram.	0.6000 gram.	0.6000 gram.	0.6000 gram.
Volume of N found,	102.0 cc.	101.5 cc.	102.0 cc.	101.8 cc.
Weight of N found,	0.1282 gram.	0.1275 gram.	0.1281 gram.	0.1279 gram.
Per cent. of N found[1]	21.36 per ct.	21.25 per ct.	21.35 per ct.	21.32 per ct.
Per ct. of N corrected[2]	21.24 "	21.16 "	21.29 "	21.25 "

The average percentages of nitrogen in the ammonium salts, as above obtained, compare with those found by combustion with soda-lime and with the theoretical percentages as below. The determinations by the soda-lime method are given in detail in another place.

TABLE VIII.

Comparative Percentages of Nitrogen.

	In Ammonium Oxalate.	In Ammonium Sulphate.
Found by absolute method,	19.77 per cent.	21.24 per cent.
Found by soda-lime method,	19.76 "	21.21 "
Theoretical,	19.72 "	21.21 "

[1] Corrected for residual air in tube, temperature and pressure.

[2] Corrected for vapor tension of KOH solution.

The following are comparative results of determinations of nitrogen in flesh (mainly muscular tissue) of fish. Those with soda-lime were made by one of us (W.),[1] those by the absolute method by Dr. Long. Neither knew the results of the other's work until after both had been recorded upon the laboratory books.

TABLE IX.

Comparison between Percentages of Nitrogen found by Soda-lime and Absolute Methods in Flesh of Fish, etc.

In Flesh of	Soda-lime.			Absolute.
	A	B	Average.	
	Per cent.	Per cent.	Per cent.	Per cent.
Fish, Mackerel, ...	5.88	5.82	5.85	5.96
" Spanish Mackerel, .	10.77	10.75	10.76	10.68
" Mascalonge, . . .	13.85	13.79	13.82	13.91
" Herring, ...	10.24	10.19	10.21	10.22
" Sheepshead, . . .	11.89	11.91	11.90	11.95
" Black Bass, . . .	14.84	14.86	14.85	14.87
Lobster, ...	11.85	11.85	11.85	11.78
Scallops, ...	10.85	10.83	10.84	10.83

The outcome of these observations, and especially the close agreement of the results obtained with the two different methods, by analysts working entirely independently of each other and with no knowledge of each other's results until they were tabulated together, persuaded us that our determinations by the soda-lime method were of sufficient accuracy to meet the demands of the investigation of the composition of animal tissues, to which they were preparatory.

At the same time we are very far from saying that we regard the soda-lime method as entirely reliable, even for protein compounds, unless all needed precautions are observed.

The recapitulation of the points here urged will come appropriately in subsequent articles, which will discuss some of the sources of error in the soda-lime method and means for avoiding them.

[1] In connection with Mr. Miles Beamer.

LII.—ON BENZOLTRISULPHONIC ACID.[1]

By C. Loring Jackson and John F. Wing.

Benzoltrisulphonic acid has been prepared up to this time only by Senhofer,[2] who made it by heating a mixture of benzol, fuming sulphuric acid, and phosphoric pentoxide to 280°–290° in a sealed tube, and studied its potassium, barium, lead, and silver salts, while in a subsequent paper[3] he made a thorough investigation of the action of melted potassic hydrate upon it—a large amount of work when the extreme difficulty of the method of preparation is considered.

Our attention was first drawn to this substance while we were trying to make potassic benzolparadisulphonate by the method of Barth and Senhofer,[4] and encountered in one preparation large well-formed crystals, giving with phosphoric pentachloride a chloride melting above 180°, which proved on analysis to be Senhofer's potassic benzoltrisulphonate. As we could find no mention of the appearance of the trisulphonate under these conditions in the papers of Barth and Senhofer,[4] Koerner and Monselise,[5] or of any other chemists who have studied the action of sulphuric acid on benzol, we searched for the cause of this abnormal result, and soon found it in the fact that we had heated the crude potassic disulphonate a second time with fuming sulphuric acid. After this a few experiments were enough to prove that the action was due to the presence of potassic sulphate, and, to our great surprise, that common sulphuric acid in presence of potassic sulphate was capable of converting a benzolsulphonic acid into the trisulphonic acid, and was as efficient in this respect as the fuming sulphuric acid.

This result, it seems to us, throws light on the beautiful method of preparing trisulphonic acids, the application of which to toluol was published by Claësson[6] in 1881, and which consists in heating

[1] Communicated by the authors from the Proceedings of the American Academy of Arts and Sciences.

[2] Annalen der Chemie **174**, 243.

[3] Wien. Acad. Ber., Ser. 2, **78**, 677.

[4] Berichte der deutsch. chem. Gesell. **8,** 1478.

[5] Gazz. Chim. 1876, 133.

[6] Berichte der deutsch. chem. Gesell. **14,** 307.

a potassic sulphonate with chlorsulphonic acid, since it makes it probable that the reaction is due to the acid potassic sulphate formed during the process, rather than to the chlorsulphonic acid itself. In a general way also our process resembles that of Neville and Winther[1] for converting the amido compounds into their monosulphonic acids by the action of heat on their acid sulphates, although it is doubtful whether the mode of action of the two processes is the same, since in ours the presence of an excess of sulphuric acid is essential.

As our process converts benzoltrisulphonic acid from one of the least into one of the most accessible of the less common aromatic compounds, we have devoted some time to its study, and in this paper, after giving the details of our preliminary experiments, and the methods for preparing the benzoltrisulphonic acid, we describe the first results that we have obtained ; which consist of the determination of the crystalline form and solubility of the potassium salt,[2] the preparation and study of the chloride, the ester, which exhibits a strange instability, the amide, with several of its metallic derivatives, and its benzoyl compound, and as this, like the corresponding compound of the benzolmonosulphamide, is an acid, its sodium and barium salts and chloride with the phenylamidine derived from it, the anilid, and finally the proof by two different methods that the benzoltrisulphonic acid has the symmetrical constitution 1, 3, 5.

Formation of Benzoltrisulphonic Acid.

To prove that the presence of potassic sulphate was the cause of the formation of the trisulphonic acid, a solution of benzol in fuming sulphuric acid, to which its own volume of common sulphuric acid had been added, was divided into two equal parts (*a*) and (*b*), and, after adding a quantity of potassic sulphate to (*a*), both parts were heated in retorts under precisely the same conditions until half of the liquid had passed over. The residues were converted into potassium salts, and recrystallised, when (*a*) furnished the very characteristic crystals of the potassic benzoltrisulphonate, and gave a chloride which, after washing with ether and one crystallisation from chloroform, melted at 182° [C_6H_3 $(SO_2Cl)_3$ melts at 184°], proving that the trisulphonic acid had

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[1] Berichte der deutsch. chem. Gesell. **13,** 1940.

[2] Also some attempts to prepare substituted trisulphonic acids, which led to negative results.

been formed, while (*b*) gave a potassium salt crystallising in an asbestos-like [1] mass, which yielded a viscous chloride, from which no trace of the benzoltrisulphochloride could be obtained ; and, as both the potassic benzoltrisulphonate and its chloride are very characteristic substances, there can be no doubt that in this latter case no appreciable amount of the trisulphonic acid was formed. In a second experiment the benzolmetadisulphonic acid (made by heating the chloride with water to 150° in a sealed tube) was used, and the result was the same ; the specimen heated with sulphuric acid and potassic sulphate gave benzoltrisulphonic acid recognised as in the previous experiment, while that heated with sulphuric acid alone gave no trace of this product.

The experiments just described having proved that the presence of potassic sulphate is necessary for the formation of the trisulphonic acid, we next considered the question, "Cannot the trisulphonic acid be formed by the action of acid potassic sulphate alone without an excess of sulphuric acid ?" and found that potassic benzolmetadisulphonate fused with acid potassic sulphate remained unaltered, even at a temperature where the mass began to char. It is evident, therefore, that the potassic sulphate serves only to render the sulphuric acid more efficient, and it remained to determine by experiment, if possible, the manner of its action. Since in Senhofer's method, the only one beside ours by which the benzoltrisulphonic acid has been obtained, the action was due to the presence of a powerful dehydrating agent (phosphoric pentoxide), the most plausible theory was that the acid potassic sulphate acted simply by the removal of water. To test this hypothesis we substituted for the potassic sulphate in one experiment argentic sulphate, and in another zincic sulphate, as, if the action of the salt is due only to its attraction for water, like that of the phosphoric pentoxide in Senhofer's method, the latter should produce quite as good a result as potassic sulphate, whereas the argentic sulphate would be entirely without action. Upon heating three portions of benzolmetadisulphonic acid with the same proportion of sulphuric acid, (*a*) without the addition of a salt, (*b*) with addition of zincic sulphate, and (*c*) with addition of argentic sulphate, we found that, while no trace of the trisulphonic acid could be detected in (*a*)

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[1] We have not succeeded in determining the nature of this potassium salt. It does not resemble the potassic benzolmonosulphonate, which crystallises in glistening plates, nor have we found any disulphonate corresponding to it in properties. We hope to return to this subject hereafter.

or (*b*), it was formed in large quantity in (*c*), and, if anything, was accompanied with less of the tarry secondary products than when potassic sulphate was used, so that argentic sulphate could perhaps be used advantageously in place of potassic sulphate in the manufacture of the trisulphonic acid, since, owing to its slight solubility, it can be filtered out with little loss after the addition of water to the product of the reaction, and is then ready to use again after drying. It follows from the above results that the salt does not act as a dehydrating agent, but rather as a carrier of the sulphuric acid, owing to the formation of an acid salt.

The experiments just described have led us to the following hypothesis to explain the formation of the benzoltrisulphonate by the action of potassic sulphate and sulphuric acid; but we wish it distinctly understood that we could find no way of submitting this hypothesis to a complete experimental proof, and therefore offer it simply as the most plausible explanation of the observed facts that we have been able to find. The acid potassic sulphate formed by the sulphuric acid and potassic sulphate is first, we suppose, converted into the potassic pyrosulphate by loss of water, and the pyrosulphate in its turn decomposed by the sulphuric acid, giving potassic sulphate and fuming sulphuric acid, which, breaking up into H_2SO_4 and SO_3, furnishes the nascent sulphuric anhydride to form the benzoltrisulphonic acid, while the potassic sulphate goes through the same series of reactions again, which can be written as follows :

$K_2SO_4 + H_2SO_4 = 2KHSO_4,$

$2KHSO_4 = K_2S_2O_7 + H_2O,$

$K_2S_2O_7 + H_2SO_4 = K_2SO_4 + H_2S_2O_7 = K_2SO_4 + H_2SO_4 + SO_3.$

Of these reactions the second can be considered well established, since the proportion of acid to potassic sulphate in the mixture used by us is almost exactly one molecule of K_2SO_4 to two of H_2SO_4; and it has been found,[1] when such a solution is allowed to cool, that it deposits first the neutral salt K_2SO_4, and afterward the potassic pyrosulphate $K_2S_2O_7$. But the last reaction is certainly not above criticism, since in it sulphuric acid is made to displace pyrosulphuric acid, which last, it is fair to suppose, is the stronger of the two. In answer to this we would suggest, that the reaction either may be brought under Berthollet's law on account of the formation of the volatile sulphuric anhydride, or,

[1] Gmelin Kraut's Handbuch der Chemie, 1875, **2,** 48.

what seems to us more probable, it is brought about by the concurrent attraction of the sulphuric anhydride for the benzoldisulphonic acid. It is possible, however, that one of the two following reactions may express the action more correctly :

$$KHSO_4 + C_6H_4(SO_3H)_2 = C_6H_3(SO_3H)_2SO_3K + H_2O.$$
$$K_2S_2O_7 + 2C_6H_4(SO_3H)_2 = 2C_6H_3(SO_3H)_2SO_3K + H_2O.$$
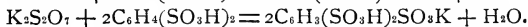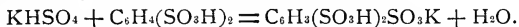
But in these reactions the excess of sulphuric acid must be supposed to act as a dehydrating agent, and thus produce the action, since we have proved experimentally that no action takes place when an excess of sulphuric acid is absent; and this observation seems to us to make these two reactions less probable than the series in which sulphuric anhydride is formed.

We have not multiplied experiments with different metallic sulphates, as it has not seemed to us that such work would throw any additional light on the theory of the process; we may mention, however, that we have also tried aluminic sulphate, which gave rise to the formation of a little trisulphonate when heated with metadisulphonic acid and sulphuric acid, but, as far as we could judge, was much less efficient in its action than the potassic sulphate.

Preparation of Benzoltrisulphonic Acid.

As the result of many experiments we have worked out the following process for preparing benzoltrisulphonic acid from potassic benzolmetadisulphonate. 15 grams of potassic benzolmetadisulphonate, which need not be freed from its water of crystallisation, are mixed in a porcelain dish with 18 grams of common strong sulphuric acid,[1] and heated with the free flame, care being taken to avoid heating the edges of the liquid too intensely during the first stage of the process, as at this time there is danger of charring. After the salt has dissolved, the sulphuric acid begins to come off in heavy white fumes, but without the formation of bubbles; in fact, there is no bumping or tumultuous evolution of vapor in any part of the process. If the operation is stopped at this point, the disulphonate will be found unaltered. After heating for a few minutes, little bubbles appear in large numbers, and soon after the mass becomes pasty, and begins to puff up, while the evolution of fumes slackens; at this point the lamp is to be removed. The product, if

[1] Double these quantities can be used, but it is not convenient to work with much larger quantities than 30 grams at a time. The benzolmetadisulphonate may contain a small quantity of potassic carbonate or sulphate without injury to the process, but should be free from colored tarry impurities.

charring was avoided in the early part of the process (there is little danger of it later), is of a reddish brown color, and almost completely solid. The loss in weight should be about 7 grams, and the whole operation takes little more than fifteen minutes. After the residue is cold, it is dissolved in water, and treated with an excess of baric carbonate to remove sulphuric acid, when the greater part of the colored impurity is carried down by the baric sulphate, so that the filtrate is usually of a pale wine-yellow. The precipitate should be boiled out with water once or twice, and the washings added to the filtrate, which, after converting any barium salt into potassic trisulphonate by potassic sulphate, is evaporated until its surface after cooling is covered with little crystals, when it usually deposits fine crystals after a short time, which can be increased in size by the spontaneous evaporation of part of the mother liquor, and purified by recrystallisation from boiling water. The mother liquors, when sufficiently concentrated, solidify to a brownish pasty mass of a finely granular consistency, filled with larger crystals of potassic benzoltrisulphonate, which can be separated mechanically by scraping with a flat-pointed platinum stirrer the semi-liquid finer grained impurity through the holes in a perforated platinum cone placed in a funnel. The larger crystals left behind are then purified by crystallisation from water. The yield from this process can be raised by careful work to 44 per cent. of the theoretical yield, and it is possible to increase it still further by boiling the precipitate formed by baric carbonate with a solution of potassic carbonate, as the baric benzoltrisulphonate is very sparingly soluble in water. We cannot recommend this treatment, however, as the potassic benzoltrisulphonate extracted in this way is contaminated to such an extent with the colored impurities carried down by the precipitate of barium salts, that it is very hard to obtain white and pure crystals from it; in fact, it is easier to prepare fresh from the benzolmetadisulphonate.

The benzoltrisulphonic acid can also be prepared from benzol without isolating the lower sulphonic acids, and this method is sometimes convenient when large quantities of the substance are desired; but it is decidedly inferior to that just described, for two reasons, first, because the yield is very much smaller, and, second, a certain amount of benzolparadisulphonate is formed, which it is not easy to separate from the trisulphonate by crystallisation. For this purpose 100 (or more) grams of benzol are dissolved in the

same volume of common sulphuric acid by boiling them together in a flask with a reverse cooler;[1] when the solution is complete, the product is mixed with its own volume of common sulphuric acid and between 60 and 70 grams of potassic sulphate, and distilled in an untubulated retort till about one-third of the total amount of sulphuric acid used has passed over. The liquid boils quietly without bumping. The residue is then divided into two parts, and these are heated in porcelain dishes precisely as in the previous process. The product is much more impure than when made from the potassic disulphonate, and it is better therefore to decolorise it by treatment with plumbic oxide after a part, but not the whole, of the large excess of sulphuric acid has been removed by marble or baric carbonate, since the greater part of the coloring matter is precipitated on adding an excess of plumbic oxide if the solution is acid, and still more comes down with the plumbic carbonate when potassic carbonate is added to the filtrate ; but if the solution is thoroughly neutralised by the marble, very little, if any, of the colored impurity comes down with the lead salts, and in that case it is very hard to get rid of it. The yield was very small, and, although we could have raised it undoubtedly by working up the insoluble residues, we have never tried to do so, because we have found it easier to prepare a fresh portion than to purify the highly colored salts which would be obtained in this way. It is advisable, however, to heat once more with sulphuric acid the brown impure residues left by the evaporation of the mother liquors, from which no more crystals of benzoltrisulphonate can be separated, as in this way an additional quantity of the trisulphonate can be obtained. We have tried also to purify the impure residues left after the removal of the crystals by treatment with phosphoric pentachloride, and washing the product with ether or chloroform, but have obtained only unsatisfactory results.

The secondary products formed in this process are of little or no interest. They consist principally of a dark reddish brown to black substance giving a potassium salt of tarry consistency more soluble than the potassic benzoltrisulphonate, which it will not be easy to purify. There appears also on evaporation of the mother liquors a dark-colored granular potassium salt, whose viscous chloride solidifies after standing for some weeks, and it is then possible to obtain much benzoltrisulphochloride from it by treatment with chloroform ; it is probable, therefore, that it consists

[1] Michael and Adair, Berichte der deutsch. chem. Gesell. **10**, 585.

principally of the benzoltrisulphonate prevented from crystallising by the presence of the dark-colored impurity just mentioned, or of some potassic benzolmetadisulphonate.

If the trisulphonic acid was made direct from the monosulphonic acid, some benzolparadisulphonic acid was also formed, which made the purification of the benzoltrisulphonate by crystallisation more difficult. It was recognised by the melting point of its chloride, 139°, whereas Koerner and Monselise[1] give 131°, and the following analysis of the chloride dried at 100° :

0.1008 gram of substance gave, after decomposition by boiling with a solution of pure sodic carbonate, 0.1054 gram of argentic chloride.

	Calculated for $C_6H_4(SO_2Cl)_2$.	Found.
Chlorine	25.82	25.86

We are inclined to consider the melting point (139°) given by us for the benzolparadisulphochloride as more accurate than that of Koerner and Monselise (131°), since their product was prepared from a mixture of the para and meta compounds, and a small quantity of the latter, melting at 63°, would have been enough to lower the melting point very considerably, and its presence could not be determined by analysis ; the impurity in our product, on the other hand, would have been benzoltrisulphochloride, and that there could have been no appreciable amount of this substance present is shown conclusively by our analysis.

Benzoltrisulphonic Acid and its Salts.

We have little to add under this head to the excellent work of Senhofer. The free acid, when heated, became charred, and gave off a smell like caramel ; but the soluble part of the residue consisted of the unaltered acid, as was shown by the crystalline form of its potassium salt and the melting point of its chloride. The experiment gave so little promise of interesting results that it was not repeated on a larger scale. The following analysis of the free acid dried at 100°, which it was necessary to make in the course of our work, confirms Senhofer's statement that it retains three molecules of water at that temperature.

0.3772 gram of the acid dried at 100° gave by the method of Carius 0.7004 gram of baric sulphate.

	Calculated for $C_6H_3(SO_5H)_3 \, 3H_2O$.	Found.
Sulphur	25.80	25.51

[1] Gaz. Chim. 1876, 140.

We add also an analysis of the potassium salt, which yielded the same amount of water of crystallisation (three molecules) as given by Senhofer; but, whereas he states that only one and a half molecules of the water are given off at 100°, we found that the whole was evolved at this temperature.

0.3768 gram of air-dried salt at 100° lost 0.0431 gram.

	Calculated for $C_6H_3(SO_3K)_3 3H_2O$.	Found.
Water	11.11	11.43

0.7404 gram of dry salt gave 0.442 gram of potassic sulphate.

	Calculated for $C_6H_3(SO_3K)_3$.	Found.
Potassium	27.13	26.80

We have determined the solubility of the potassium salt as follows:

I. 3.6594 grams of a solution of $C_6H_3(SO_3K)_3$ saturated at 20° left on evaporation 1.3074 grams of the salt dried at 260°.

II. 2.034 grams of the solution gave 0.716 gram of the dried salt.

Therefore a saturated solution of potassic benzoltrisulphonate at 20° contains the following percentages of the salt free from water of crystallisation:

I.	II.
35.72	35.21

Dr. O. W. Huntington has at our request determined the crystalline form of the potassium salt $C_6H_3(SO_3K)_3 3H_2O$, and kindly furnishes us with the following statement:
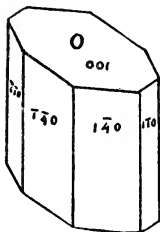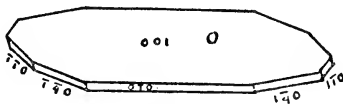

FIG. 1.

FIG. 2.

"Monoclinic, with marked variation of type. As no planes were observed except the basal plane and vertical domes, and pinacoids, it was impossible to make a complete determination of the crystal. The following measurements were obtained:

$$001 \wedge \bar{1}10 = 65° \ 28'$$
$$1\bar{1}0 \wedge 110 = 50° \ 55'$$
$$1\bar{1}0 \wedge \bar{1}40 = 24° \ 40'$$
$$\bar{1}40 \wedge 1\bar{4}0 = 79° \ 45'$$

Most of the faces of the crystals were uneven, and the angles printed in heavy type are the only ones which could be measured with accuracy.

" From these angles the inclination of the axes and the ratio of the ortho diagonal to the clino axis may easily be calculated.

$$\beta = 68° \ 38' \ 30'' \qquad\qquad a : b = 1 : 2.10.$$

The crystals vary between the form shown in Fig. 1 and that of Fig. 2. In the second form the clino pinacoid is a characteristic feature which is absent in crystals of the first type, and the forms of both types run out into needles, in one case parallel to the vertical axis, and in the other parallel to the clino diagonal."

The potassium salt is not acted on by a cold solution of potassic permanganate, but, if heated with it, is oxidised, and we were unable to find any organic matter in the product.

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The following attempts were made to obtain substituted benzoltrisulphonic acids. The silver salt was made by boiling the chloride with argentic oxide and water, and to the filtered solution bromine was added in order to make brombenzoltrisulphonic acid by the method of Nölting and Plawski,[1] which has been proved to be of wide application to monosulphonic acids by Limpricht.[2] A heavy precipitate of argentic bromide was formed at once, but the filtrate after being freed from compounds of bromine by evaporation gave a chloride melting at 184°, the melting point of benzoltrisulphochloride. It was analysed also, as it was barely possible that the brombenzoltrisulphochloride might melt at the same temperature as the non-substituted compound.

0.2374 gram of the substance gave 0.2718 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2Cl)_3$.	Found.
Chlorine	28.52	28.32

The argentic benzoltrisulphonate, therefore, is affected by bromine in an entirely different way from the monosulphonates. The

[1] Berichte der deutsch. chem. Gesell. **8**, 819.   [2] Annalen der Chemie **186**, 134.

filtrate before evaporation contained bromic acid, as was proved by the following experiments. Some of the filtrate containing no free bromine gave no precipitate when argentic nitrate was added, but upon boiling with alcohol a heavy precipitate of argentic bromide was formed; to another portion of this filtrate potassic iodide was added, when iodine was set free in large amount. The reaction must run as follows:

$$C_6H_3(SO_3Ag)_3 + 3Br_2 + 3H_2O =$$
$$3AgBr + C_6H_3(SO_3H)_3 + HBrO_3 + 2HBr.$$
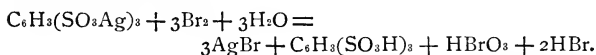
Iodine acts on the argentic benzoltrisulphonate in a similar way. We have tried also to obtain a bromine compound by heating the potassium salt with bromine to 140° for sixteen hours, and also by heating it dissolved in strong sulphuric acid with bromine; but in neither case was hydrobromic acid given off, the trisulphonic acid remaining unaltered. It is possible, however, that longer heating with bromine might produce the desired result.

Our attempts to obtain a nitro acid were no more successful than those to make the bromine acid, as the potassic benzoltrisulphonate can be boiled with fuming nitric acid, or even with a mixture of fuming nitric acid and sulphuric acid, for over an hour without undergoing any alteration. When, however, the chloride is heated to 140° for sixteen hours with a large excess of fuming nitric acid, it is converted into a new substance with the most uninviting properties, which we have not studied further because sulphuric acid is eliminated in the process, and we propose to confine our attention to the trisulpho compounds.

Benzoltrisulphochloride, $C_6H_3(SO_2Cl)_3$.

This substance is prepared by heating potassic benzoltrisulphonate, previously dried at 150°, with a little more than the calculated amount of phosphoric pentachloride (10 parts of the salt to 15 of the pentachloride) in a test-tube or flask to 150° in an air-bath. If the substances are heated in a dish there is little or no action. After the phosphoric oxychloride has distilled off, the product is treated with water, and finally warmed with it, but this warming should not be long continued, as the trisulphochloride is much more easily attacked by hot water than the benzolmetadisulphochloride. After washing the chloride thoroughly with warm water, it is purified by crystallisation from boiling chloroform. The

yield was between 80 and 90 per cent. of the theoretical. Samples contaminated with lower sulphochlorides often can be freed from them by washing with ether. The substance dried at 100° gave the following results on analysis :

I. 0.2984 gram gave, after decomposition by boiling with a solution of potassic hydrate, 0.3488 gram of argentic chloride.

II. 0.1300 gram treated in the same way gave 0.1530 gram of argentic chloride.

III. 0.2374 gram gave, after decomposition with a boiling solution of pure sodic carbonate, 0.2718 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2Cl)_3$.	I.	Found. II.	III.
Chlorine	28.52	28.90	29.10[1]	28.32

Properties.—The benzoltrisulphochloride crystallises from chloroform in little silky flattened needles, which under the microscope are seen to have the ends bevelled, or occasionally terminated by two planes forming an obtuse angle ; frequently groups are observed made up of a number of needles united longitudinally, giving a characteristic comb-like appearance to the ends. Out of benzol it forms good-sized plates, apparently belonging to the triclinic system. It melts at 184° (uncorr.), and sublimes with some difficulty at temperatures above 200°, forming good-sized flattened needles similar in shape to the crystals from benzol. It is insoluble in water, hot or cold, but is slowly decomposed and dissolved when boiled with it ; very slightly soluble in cold alcohol or methyl alcohol, but freely dissolved with decomposition when boiled with them ; very slightly soluble in ligroin, slightly soluble in ether, freely in benzol, carbonic disulphide, glacial acetic acid, or chloroform. Chloroform is the best solvent for it, as it is much more soluble in it when hot than when cold. As already mentioned, the chloride is slowly converted into the acid by boiling water, and is much more easily attacked in this way than the benzolmetadisulphochloride, so that the acid can be prepared conveniently by heating it with water in open vessels, whereas with the di compound this reaction does not take place readily at temperatures below 140°. With boiling alcohol the product is also the acid ; but this point will be discussed more fully under the ester. Solutions of potassic hydrate or carbonate, or a mixture of argentic oxide and water, when boiled with the chloride, convert it quickly and

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[1] The potassic hydrate used in I and II was not perfectly free from potassic chloride.

easily into the corresponding salt. The study of the action of reducing agents on the chloride will be reserved for a future paper.

Benzoltrisulphonic Ester, $C_6H_3(SO_3C_2H_5)_3$.

This substance was prepared by the action of ethyl iodide on argentic benzoltrisulphonate, made by boiling the chloride with argentic oxide, and after filtering out the argentic chloride and excess of argentic oxide, evaporating to dryness on the water-bath, and drying at 100°. The ethyl iodide acts on the silver salt with violence even in the cold, so that the process must be carried on in a flask with a return condenser, and, after it has come to an end, which can be made sure by heating for a short time on the water-bath, the product is extracted with ether, and the extract purified by crystallisation from benzol, and dried in vacuo. Ethyl bromide may be used instead of ethyl iodide, but in this case the mixture must be heated to 100° in a sealed tube to obtain complete action.

The ester can also be prepared by the action of benzoltrisulpho-chloride, mixed with a large excess of benzol, on the proper amount of sodic ethylate made from as little alcohol as possible ; but this method is not so good as the preparation from the silver salt and ethyl iodide. If the attempt is made to prepare the ester by the action of sodic ethylate dissolved in alcohol upon the benzoltrisulphochloride, the product is sodic benzoltrisulphonate, or, if absolute alcohol is substituted for sodic ethylate, benzoltrisulphonic acid, the ester at first formed being afterward decomposed by the absolute alcohol, according to the reaction given under the properties of the ester. The ester cannot be made by the action of hydrochloric acid gas on an alcoholic solution of the trisulphonic acid. The composition of the ester dried in vacuo was determined by the following analysis :

I. 0.2646 gram of the substance gave by the method of Carius 0.4662 gram of baric sulphate.

II. 0.156 gram of the substance gave 0.2719 gram of baric sulphate.

	Calculated for $C_6H_3(SO_3C_2H_5)_3$.	I.	II.
		Found.	
Sulphur	23.88	24.16	23.94

Properties.—The benzoltrisulphonic ester forms well-developed shining white crystals, often more than a centimeter long, which belong to the triclinic system ; a careful measurement of their

angles was, however, impossible, because we could not obtain them with smooth enough faces. It melts at 147°, but if heated for some time to 110° is decomposed, leaving a residue of the benzoltrisulphonic acid ; the reaction which takes place is probably the following :

$$C_6H_3(SO_3C_2H_5)_3 = C_6H_3(SO_3H)_3 + 3C_2H_4,$$

as 0.1674 gram of substance lost 0.0324 gram.

Calculated for a loss of $3C_2H_4$.	Found.
20.89	19.36.

It is essentially insoluble in water, freely soluble in ether, chloroform, carbonic disulphide, or benzol—the last being the best solvent for it—insoluble in ligroin, decomposed and dissolved by glacial acetic acid, dissolves freely in alcohol, but is decomposed by it, as upon evaporating the solution, even if absolute alcohol is used, the benzoltrisulphonic acid is left. This reaction seemed to us so curious that we studied it more carefully, as follows. 10 grams of benzoltrisulphochloride were boiled in a flask with a reverse cooler with 12 grams of absolute alcohol ; after half an hour the solid had completely dissolved, and upon examining the flask it was found that much hydrochloric acid had been formed, also apparently a little ethyl chloride due to a secondary reaction, but no ethylene could be detected. The contents of the flask, after being freed from hydrochloric acid with potassic hydrate, were distilled fractionally with a Hempel's column, when it appeared that the principal product of the reaction was ethylether, recognised by its boiling point, 35°, and by its smell. The following reactions, therefore, probably take place :

I. $C_6H_3(SO_2Cl)_3 + 3C_2H_5OH = C_6H_3(SO_3C_2H_5)_3 + 3HCl$;
II. $C_6H_3(SO_3C_2H_5)_3 + 3C_2H_5OH = C_6H_3(SO_3H)_3 + 3(C_2H_5)_2O$;

and the action is exactly analogous to the ordinary method of making ethyl ether. Methyl alcohol seems to act on the ester in the same way as ethyl alcohol—the residue left after evaporating a methyl alcohol solution of it being benzoltrisulphonic acid. The ester was not acted on in the cold by sodium or sodic ethylate.

Benzoltrisulphamide, $C_6H_3(SO_2NH_2)_3$.

This substance was made by adding a very strong solution of ammonia to the benzoltrisulphochloride and allowing the mixture to

stand a short time. It was purified by crystallisation from boiling water. It can be formed also by the action of ammonic carbonate on the chloride, but the result was less satisfactory than with the solution of ammonia. The mother liquors from the crystallisation contain a quantity of ammonic benzoltrisulphonate, which, after conversion into the potassium salt by boiling with potassic hydrate, can be reconverted into the chloride. The substance dried at 100° gave the following results on analysis:

I. 0.2358 gram of substance gave after heating with soda-lime 0.1162 gram of ammonic chloride.

II. 0.3739 gram of substance gave, according to the method of Carius, 0.8318 gram of baric sulphate.

	Calculated for $C_6H_3(SO_2NH_2)_3$.	Found.	
		I.	II.
Nitrogen	13.33	12.89	...
Sulphur	30.47	...	30.56

Properties.—The benzoltrisulphamide crystallises from boiling water in shining flattened needles with very sharp ends, sometimes nearly a centimeter long. It can also be obtained from water in square prisms with oblique ends, apparently of the monoclinic system, or in rhombic plates. From alcohol it crystallises in long slender needles. Its melting point is 310°–315° (uncorr.); it is only slightly soluble in cold water, as shown by the following determination of its solubility:

I. 12.367 grams of the solution saturated at 25° gave on evaporation 0.0172 gram of the amide.

II. 11.164 grams of the solution gave 0.0186 gram of the amide.

The solution of the benzoltrisulphamide saturated at 25° contains, therefore,

| I. | II. |
| 0.14 per cent. | 0.17 per cent. |

It is much more freely soluble in boiling water than it is in cold, and this is the best solvent for it; soluble in alcohol, rather more so in methyl than in common alcohol; not very soluble in benzol; insoluble, or nearly so, in ether, ligroin, chloroform, or glacial acetic acid either hot or cold. The amide is much more soluble in a solution of ammonia than in water, but it is thrown down unaltered when the ammonia is driven off from such a solution by heat; it also dissolves very easily in a solution of potassic hydrate, and this solution is not decomposed, even when it is boiled for a

short time. The hot aqueous solution of the amide gives a white precipitate with mercuric nitrate, but none with mercuric chloride ; a difference in behavior which is not surprising when it is remembered how differently these two reagents act with acid sodic carbonate, sodic phosphate, oxalic acid, and even water. The composition of the precipitate formed with mercuric nitrate is discussed below. The hot solution of the amide also gives with mercurous nitrate a white precipitate, which becomes gray on standing, but no precipitate with solutions of the salts of any of the other common metals.

The *Silver Salt*, $C_6H_3(SO_2NHAg)_3$, was made by adding argentic nitrate to a hot solution of the amide, and then ammonic hydrate, but not in excess, as this dissolves the precipitate ; if by accident an excess has been added, the precipitate can be obtained again by boiling off the ammonia. The flocculent white precipitate thus formed was washed with water, dried in vacuo, and analysed.

0.2778 gram of the salt gave by precipitation from its solution in dilute nitric acid 0.1886 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2NHAg)_3$.	Found.
Silver	50.94	51.11

It is a tolerably stable white powder, insoluble in water, soluble in nitric acid or ammonic hydrate. When a little tincture of iodine is added, the silver is converted into argentic iodide. Compare the analogous reaction with mercuric salt.

Mercuric Salts of Benzoltrisulphamide.—When the amide is boiled with yellow mercuric oxide suspended in water, a white precipitate is formed, the composition of which varies according to the proportion of oxide and amide used.

$C_6H_3(SO_2NHHgOH)_3$.—To prepare this salt, 0.65 gram of mercuric chloride was converted into the oxide by precipitation with sodic hydrate, and the washed but not dried oxide boiled with a solution of 0.25 gram of the amide. The action takes place very slowly even under these conditions (much more slowly and imperfectly if the oxide has been dried) ; but after boiling for twenty-four hours it was nearly complete, although there were still a few yellow specks of oxide visible. These were separated mechanically, as far as possible, and the precipitate washed and dried at 100° ; its analysis is given under I. The same salt is

obtained much more conveniently by adding a solution of mercuric nitrate to a boiling solution of the amide, and washing with boiling water. An analysis of the salt thus prepared, and dried at 100°, is given under II. It is probable that the mercuric nitrate forms at first the compound $C_6H_3(SO_2NHHgNO_3)_3$, and that this is decomposed by the hot water in the same way that mercuric nitrate itself is. We do not pretend to determine, however, whether the hydroxyl is attached to the mercury or to the nitrogen, which in the latter case would be in the quinquivalent condition.

I. 0.299 gram of substance dissolved in hydrochloric acid and treated with sulphuretted hydrogen gave 0.2164 gram of mercuric sulphide.

II. 0.2756 gram of substance gave 0.1994 gram of mercuric sulphide.

	Calculated for $C_6H_3(SO_2NHHgOH)_3$.	I.	II.
		Found.	
Mercury	62.30	62.38	62.38

$[C_6H_3(SO_2NH)_3]_2Hg_3$.—This salt was prepared like the preceding, by boiling the moist mercuric oxide from 0.65 gram of mercuric chloride with 0.5 gram of the amide in aqueous solution. Even greater difficulties were encountered than in the preceding case, the reaction taking place as slowly, and being less complete ; on this account we have not succeeded in preparing the substance in a state of purity, as the following analysis shows ; the difference is due to a slight excess of mercuric oxide, which could not be removed, but the result is near enough to leave no doubt about the formula of the compound.

0.3416 gram of substance dried at 100° gave 0.2056 gram of mercuric sulphide.

	Calculated for $[C_6H_3(SO_2NH)_3]_2Hg_3$.	Found.
Mercury	49.02	51.88

Both substances are white powders, insoluble in water, soluble in hydrochloric acid, which form mercuric iodide when boiled with water and iodine for some time ; the filtrate, however, contains no organic substance except unaltered benzoltrisulphamide.

The aqueous solution of the amide boiled with plumbic oxide formed white flocks, but the action took place with so much difficulty that we did not try to prepare the substance for analysis. With cupric oxide we could observe no action. A solution of the sulphate of cuprammonium took up the amide with great avidity,

forming a dark blue solution, which deposited azure blue disks of so deep a tint as to look nearly black, while the mother liquor showed only a very pale blue color. The solid was but sparingly soluble in water, being decomposed by it, but tolerably stable in the dry state ; dissolved in dilute hydrochloric acid, it gave no precipitate with baric chloride. It was dried in a desiccator, and its composition determined by the following analyses :

I. 0.1628 gram of substance dissolved in hydrochloric acid and precipitated with sodic hydrate gave 0.0356 gram of cupric oxide.

II. 0.2564 gram gave 0.0596 gram of cupric oxide.

	Calculated for $[Cu(NH_3)_4]_3[(SO_2)_3C_6H_3]_2$.	Found. I.	II.
Copper	18.57	17.46	18.57

No better agreement between these results could be expected, when it is remembered that the substance could not be recrystallised. It is evidently cuprammonic benzoltrisulphonate, but we were unable to prepare it by the action of cuprammonic sulphate on a solution of potassic benzoltrisulphonate.

Several attempts to obtain the *imide*, $[C_6H_3(SO_2)_3]_2(NH)_3$, although they led to no definite results, may be mentioned here. The benzoltrisulphochloride mixed with absolutely dry benzol and the silver salt of benzoltrisulphamide, and heated to 100° in a sealed tube for two days, remained entirely unaltered. The experiment could not be repeated at a higher temperature for fear of decomposing the silver salt. If the chloride was heated with the amide, in the proportion of one molecule of each, to 190°, there was no action ; but if the temperature was raised to 200°–210°, and maintained at this point for some hours, hydrochloric acid was given off, and a black product formed, which, when treated with cold water, swelled up to a gelatinous mass, the water becoming acid with hydrochloric acid. The jelly thus obtained, after being thoroughly washed with water, dried to a more or less colored powder, insoluble in all the solvents that we have tried, so that we have not been able to purify it properly for analysis. Some nitrogen determinations made with a substance extracted with all the common solvents gave results not far removed from the numbers required by the imide ; but they are entitled to little, if any, confidence, as the substance still contained some chlorine. We satisfied ourselves by a special experiment that the substance mentioned above was not formed from the benzoltrisulphamide alone, since

the amide was not altered by heating it to a temperature of 230°
for an hour and a half.

Benzoylbenzoltrisulphamide, $C_6H_3(SO_2NHCOC_6H_5)_3$.

Benzoyl chloride has no action on benzoltrisulphamide when the
two substances are heated together on the water-bath ; if, however,
the mixture of these substances in the proportion of three mole-
cules of the chloride to one of the amide (1.3 gram to 1 gram) is
heated in a flask with a return cooler to 140° by means of an
oil-bath, hydrochloric acid is given off, and the benzoyl derivative
is formed. During the process great care must be taken that the
temperature does not rise above 150°, as at a point but little above
this (150°–180°) decomposition sets in, and in that case the prin-
cipal product of the action is kyaphenine. After the action has
come to an end, which usually takes from five to seven hours, the
product is extracted with benzol to remove any undecomposed
benzoyl chloride, and purified by crystallisation from hot alcohol.
Dried at 100° it gave the following results on analysis :

I. 0.2234 gram of substance gave 13.3 cc. of nitrogen under a
pressure of 766 mm. and at a temperature of 22°.

II. 0.1632 gram of substance gave by the method of Carius
0.1784 gram of baric sulphate.

	Calculated for $C_6H_3(SO_2NHC_7H_5O)_3$.	I.	Found. II.
Nitrogen	6.69	6.79	
Sulphur	15.31	...	15.02

Properties. — Benzoylbenzoltrisulphamide crystallises from
alcohol in rather short and stout well-formed prisms, with an
unmodified basal plane, which seem to belong to the hexagonal
system. It has no definite melting point, since it decomposes at
comparatively low temperatures (below 200°), and the melting
point is therefore modified by the length of time during which the
substance has been heated. The highest point which we have
observed is 285°, but this can be materially modified by altering
the conditions under which the melting point is taken ; for instance,
two tubes were filled with portions of the same preparation, and
one of them was allowed to hang in the bath in the usual way,
when it melted at 264°, while the other, which was not allowed to
remain in the bath, but only dipped into it occasionally, did not
melt till 275°. The two observations were made at the same time,

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so that in all other respects the conditions were the same. The melting is accompanied with blackening and effervescence. By long-continued heat at temperatures between 150° and 180° the substance is completely decomposed, giving kyaphenine as the principal product, which was recognised by its melting point, 230° (Pinner and Klein[1] give 231°). The decomposition is undoubtedly similar to that of the corresponding mono compound, which, according to Wallach and Gossmann,[2] gives kyaphenine or benzonitrile and benzolmonosulphonic acid. The benzoyl compound .early insoluble in water, whether hot or cold, but not absolutely so, as a moist crystal, after being boiled with water, if laid upon litmus paper, gives an acid reaction. It is tolerably soluble in alcohol or methyl alcohol, especially when boiling, nearly insoluble in ether, chloroform, or glacial acetic acid, essentially insoluble in ligroin, benzol, or carbonic disulphide. It is easily soluble in sodic, ammonic, or baric hydrates, or in sodic carbonate; hydrochloric acid precipitates the original substance from these solutions. The solution in ammonic hydrate, if evaporated to dryness on the water-bath, leaves a colorless varnish, which dissolves again in water; this solution, however, gives no characteristic precipitates with the common reagents, although we may mention the white precipitates produced by argentic nitrate and basic plumbic acetate (neutral plumbic acetate gives no precipitate). We have studied the sodium and barium salts, and intended also to analyse the silver salt, but found that it was too soluble to be purified conveniently by washing, and came down from its hot aqueous solution as a varnish.

Sodic Benzoylbenzoltrisulphamide, $C_6H_2(SO_2NNaC_7H_5O)_3.$ — This salt was made by boiling a solution of the calculated amount of sodic carbonate with benzoylbenzoltrisulphamide, and evaporating to dryness, finally spontaneously. Upon drying at 100° it lost varying amounts of water, but in no case so much as one molecule; we are therefore inclined to think it was only hygroscopic water, as the salt was of a varnish-like consistency, which would offer great resistance to air-drying.

0.2466 gram of the salt dried at 100° gave 0.0794 gram of sodic sulphate.

	Calculated for $C_6H_3(SO_2NNaC_7H_5O)_3.$	Found.
Sodium	9.95	10.43

[1] Berichte der deutsch. chem. Gesell. **11**, 764.   [2] Ibid. **11**, 754.

The salt is a white varnish, which we did not succeed in obtaining in crystals; it dissolves in water very slowly, but does not need a large amount for complete solution. The solution is neutral, and we did not succeed in preparing an acid salt, as when the free benzoylbenzoltrisulphamide was boiled with one molecule of sodic carbonate, nearly two-thirds of the amide remained undissolved, and the solution was barely acid.

Baric Benzoylbenzoltrisulphamide, $[C_6H_3(SO_2NC_7H_5O)_3]_2Ba_3$ $12H_2O.$—This salt was made by boiling the benzoylbenzoltrisulphamide with a solution of baric hydrate, and removing the excess of baric hydrate with carbonic dioxide. The solution was evaporated at last spontaneously.

I. 0.3192 gram of the air-dried salt dried at 100° lost 0.0372 gram.

II. 03406 gram at 120° lost 0.0408 gram.

	Calculated for $[C_6H_3(SO_2NC_7H_5O)_3]_2Ba_3\ 12H_2O.$	Found. I.	II.
Water	11.53	11.65	11.97

The air-dried salt loses in vacuo 3.66 per cent., which corresponds to $3\frac{1}{2}$ molecules of water (calculated 3.36 per cent.).

I. 0.2820 gram of the dry salt gave 0.1184 gram of baric sulphate.

II. 0.2998 gram gave 0.1214 gram of baric sulphate.

	Calculated for $[C_6H_3(SO_2NC_7H_5O)_3]_2Ba_3.$	Found. I.	II.
Barium	24.77	24.69	23.80

It forms a white varnish soluble in water.

Chloride of Benzoylbenzoltrisulphamide, $C_6H_3(SO_2N=CCl$ $C_6H_5)_3.$—This substance was made by heating the benzoylbenzoltrisulphamide with phosphoric pentachloride. Equal weights of the two substances were used, and they were heated in an open test tube by means of an air-bath at 110°. After one hour the reaction was complete, and the product was purified by washing it with ligroin, and afterward with absolute ether, which converts it from a viscous liquid to a powder. It was dried at 100° and analysed.

I. 0.2314 gram of substance gave, after boiling with a solution of pure sodic carbonate, 0.1514 gram of argentic chloride.

II. 0.2502 gram of substance gave 0.1614 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2NCClC_6H_5)_3.$	Found. I.	II.
Chlorine	15.61	16.17	15.95

Properties.—It forms colorless cubic crystals, which, like the benzoyl compound from which they are derived, show no definite melting point ; they begin to decompose at 225°, and become liquid in the neighborhood of 245°, but the melting point may vary as much as 30°. The substance is insoluble in water, benzol, ligroin, and chloroform, somewhat soluble in ether.

Benzoltrisulphobenzenylphenylamidine, $C_6H_2[SO_2N=C(NHC_6H_5)C_6H_5]_3$.—The chloride just described was converted by warming it gently with aniline into a viscous mass, which solidified after long standing. The substance was purified by washing with water, ether, and benzol, and then crystallising from hot alcohol until it showed a constant melting point. It was then dried at 100° and analysed.

0.1658 gram of substance gave 14.1 cc. of nitrogen at a pressure of 760 mm. and a temperature of 20°.

	Calculated for $C_6H_2(SO_2N_2C_{13}H_{11})_3$.	Found.
Nitrogen	9.86	9.73

Properties.—It forms white needles, which melt at 196° (uncorr.), and are insoluble in water and ligroin, soluble with difficulty in alcohol, which, however, is the best solvent for it, soluble in ether, benzol, and chloroform.

A number of attempts to make the dibenzoylbenzoltrisulphamide, $C_6H_2[SO_2N(C_7H_5O)_2]_3$, led to no result. The substance was not formed when the sulphamide was heated to 140° with six molecules of benzoyl chloride instead of three, or when the sodium salt of the benzoylbenzoltrisulphamide was heated to 150° for a day with an excess of benzoyl chloride, or when the silver salt of the benzoylbenzolsulphamide (made by adding argentic nitrate to the sodium salt) was heated to 100° in a sealed tube with an excess of benzoyl chloride. In every case the monobenzoylbenzoltrisulphamide remained unaltered.

Benzoltrisulphanilid, $C_6H_2(SO_2NHC_6H_5)_3$.

This substance was prepared by warming benzoltrisulphochloride with aniline. The product was boiled out with water, and purified by crystallisation from alcohol. Dried at 100°, it gave the following result on analysis :

0.2408 gram of the substance gave, according to the method of Carius, 0.315 gram of baric sulphate.

	Calculated for $C_6H_2(SO_2NHC_6H_5)_3$.	Found.
Sulphur	17.68	17.97

Properties.—It forms good-sized short, thick, white prisms, which melt at 237°, and are very slightly soluble in boiling water, soluble in alcohol, ether, benzol, or acetone, but insoluble in ligroin.

Constitution of Benzoltrisulphonic Acid.

We have determined the constitution of the acid in the two following ways.

First Method.—Dry potassic benzoltrisulphonate was mixed thoroughly with exactly the theoretical amount of potassic cyanide (1 gram to 0.45 gram)—if an excess of the cyanide is used, the yield is very much diminished—and heated by means of a gas furnace in a piece of combustion tubing closed at one end ; the white crystalline sublimate which collects in the cold part of the tube was removed, and saponified by boiling with alcoholic potassic hydrate, a process which lasts several days. When the evolution of ammonia ceased, the contents of the flask were acidified with hydrochloric acid, and shaken with ether ; the ether extract was an acid which melted at 320°–325°, and this melting point remained unaltered after crystallisation from water. It was converted into the silver salt, which gave the following result on analysis :

0.1528 gram of the salt gave on ignition 0.093 gram of metallic silver.

	Calculated for $C_6H_3(CO_2Ag)_3$.	Found.
Silver	61.02	60.86

No other acid could be detected in the product of the reaction. The melting points of the three tribasic acids derived from benzol are, hemimellitic acid, 185° ; trimellitic acid, 216° ; trimesic acid, above 300°. So there can be no doubt that our acid is *trimesic acid*, and therefore, if there has been no intramolecular transformation, the benzoltrisulphonic acid has the symmetrical constitution 1, 3, 5.

Second Method.—The benzoltrisulphochloride was heated with an excess of phosphoric pentachloride, according to the method of Barbaglia and Kekulé[1] for replacing a sulpho group by an atom of chlorine. For this purpose 3 grams of the chloride were sealed with 5.2 grams of phosphoric pentachloride (one molecule of the sulphochloride to six of the phosphoric pentachloride), and heated for some hours to 200°–210°. Upon treating the product with water, long needles were deposited, which were purified by

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[1] Berichte der deutsch. chem. Gesell. **5**, 875.

washing with sodic hydrate and several crystallisations from alcohol, when they melted at 63°. The yield was about 62 per cent. of the theoretical. The melting point of this substance would indicate that it is the symmetrical trichlorbenzol 1, 3, 5, which melts, according to Beilstein and Kurbatow,[1] at 63.5°. To confirm this indication we treated a portion of the substance with fuming nitric acid at a temperature of about 50°, when instead of getting the trichlormononitrobenzol of Beilstein and Kurbatow,[2] melting at 68°, we obtained a substance crystallising in long, thick prisms and melting at 130°. This observation made it necessary for us to study the action of fuming nitric acid on symmetrical trichlorbenzol, the results of which research are described fully in the following paper. It is sufficient to state here that we found the nitric acid used by us, even when acting in the cold, converted the symmetrical trichlorbenzol into the trichlordinitrobenzol, melting at 129.5°, thus proving that the trichlorbenzol derived from benzoltrisulphochloride is the symmetrical compound (1, 3, 5), and confirming the result obtained by the first method.

The study of the action of reducing agents on the benzoltrisulphochloride will be described in a subsequent paper, and Mr. G. T. Hartshorn has undertaken the extension of this method of making sulpho acids to other organic substances, obtaining results which will soon be ready for publication.

LIII.—ON THE ACTION OF NITRIC ACID ON SYMMETRICAL TRICHLORBENZOL.

By C. Loring Jackson and John F. Wing.

We were led to take up the study of this subject by our work upon the constitution of benzoltrisulphonic acid, described in the preceding paper, since the trichlorbenzol derived from that substance by replacing its sulpho groups with chlorine, although melting at 63° like the symmetrical compound (melting point 63.5° according to Beilstein and Kurbatow[3]), gave on treatment with nitric acid a body melting at 130°, whereas Beilstein and Kurbatow obtained in this way trichlormononitrobenzol,[4] melting point 68°.

[1] Annalen der Chemie **192**, 233.   [2] Berichte der deutsch. chem. Gesell. **10**, 271.
[3] Annalen der Chemie **192**, 233.   [4] Berichte der deutsch. chem. Gesell. **10**, 271.

To find the cause of this discrepancy we have prepared the symmetrical trichlorbenzol, and treated it with nitric acid in the cold, when we found that the product was the substance melting at 130° (or more accurately at 129.5°) mentioned above, which proved on analysis to be trichlordinitrobenzol. This result was the more strange, because our nitric acid had a specific gravity of only 1.505, whereas that used by Beilstein and Kurbatow showed 1.52, and in order to get their trichlormononitrobenzol we found it necessary to dilute our acid to 1.46. Since these experiments seemed to show that our nitric acid was more efficient in its action than that used by Beilstein and Kurbatow, we determined to study the subject more carefully, and next attempted the preparation of the trichlortrinitrobenzol, which we obtained without difficulty by boiling the trichlordinitrobenzol for about two hours with a mixture of our nitric acid and fuming sulphuric acid. Both this substance and the dinitro compound are new, the difficulty of the preparation of symmetrical trichlorbenzol having prevented a thorough study of this substance. On the other hand, the corresponding tribrombenzol can be made with great ease, and, as its action with fuming nitric acid has been studied frequently, we decided to extend our experiments to it to see whether in this case also our nitric acid proved more reactive than that of the chemists who have worked in this field heretofore. The complete description of our results with tribrombenzol will be postponed till a later paper, and we shall give here only that portion of them which shows that the action of our nitric acid on tribrombenzol is similar to its action on trichlorbenzol, prefacing it with a brief historical sketch of the work of our predecessors.

Koerner[1] was the first (in 1874) who studied this subject, obtaining on dissolving the symmetrical tribrombenzol with the aid of heat in nitric acid of specific gravity 1.54 the dinitro compound, with a mixture of fuming sulphuric acid and nitric acid the trinitro compound, while all his attempts to obtain the mononitro derivative by direct nitriring failed, owing to the insolubility of the tribrombenzol in weaker acid. In the next year[2] one of us[3] working in the laboratory of Berlin found that the fuming nitric

[1] Gazz. Chim. **4**, 422, 425.

[2] Von Richter (Berichte der deutsch. chem. Gesell. **8**, 1426) succeeded in obtaining the mononitro compound by boiling glacial acetic acid and tribrombenzol with nitric acid of specific gravity 1.52, but found, in agreement with Koerner, that an acid of 1.54 boiled with tribrombenzol converted it into the dinitro compound.

[3] Jackson, Berichte der deutsch. chem. Gesell. **8**, 1172.

acid supplied in that laboratory converted tribrombenzol into the mononitro compound only when boiled with it, and that it was necessary to use a boiling mixture of nitric and (common) sulphuric acids to obtain the dinitro derivative. These observations were confirmed a few years later by Wurster and Beran,[1] who obtained only the mononitro compound from the action of a nitric acid of 1.534 specific gravity alone, and the dinitro compound when its action was reinforced by mixture with crystallised fuming sulphuric acid. Even when this mixture was heated with tribrombenzol in sealed tubes to 220° for 48–60 hours, only a very minute quantity of a trinitro compound was formed ; which led them to the conclusion that the trinitro derivative mentioned but not described by Koerner could not be obtained.

In taking up again the study of the nitro compounds of symmetrical tribrombenzol we used the nitric acid of specific gravity 1.505–1.51, which had acted on trichlorbenzol in the way already described, and found that this acid converted the tribrombenzol, even when the mixture was carefully cooled, direct into tribromdinitrobenzol, no mononitro compound being formed ; and further, that by the action of a mixture of this nitric acid with fuming sulphuric acid on tribromdinitrobenzol, the tribromtrinitrobenzol, melting point 285°, was formed without difficulty in open vessels. We therefore confirm completely the results of Koerner, so far as they apply to the di and trinitro compounds, in opposition to those obtained by one of us, and by Wurster and Beran ; and, to make the comparison more striking, we have used for these experiments tribrombenzol made from some tribromaniline prepared in Berlin by one of us during his previous experiments. To sum up the whole case in a few words, it appears that our nitric acid of specific gravity 1.505–1.51 is much more efficient in its action than the commercial fuming nitric acid used in the laboratories of St. Petersburg [2] (1.52), Berlin,[3] and Munich [4] (1.534) ; and we are inclined to ascribe the high specific gravities of these commercial acids in part to the presence of lower oxides of nitrogen, while the specific gravity of our acid was due probably exclusively to HNO_3, since it was prepared in our laboratory directly from nitre and sulphuric acid, not pushing the reaction beyond the formation of acid potassic sulphate. This explanation is based upon the observation of Kolb,[5] that the specific gravity of nitric acid is raised by the

[1] Berichte der deutsch. chem. Gesell. **12**, 1821.   [2] Beilstein and Kurbatow.
[3] Jackson.   [4] Wurster and Beran.   [5] Ann. Chim. Phys., ser. 4, **10**, 137.

solution of nitric dioxide in it; and although we cannot submit it to direct experimental proof, since commercial fuming nitric acid is not to be had in this country, yet the following examination of a nitric acid similar to that used in foreign laboratories makes it exceedingly probable that this explanation is correct. This acid was prepared by distilling common nitric acid twice with an excess of sulphuric acid; it had a decided yellow color, and a specific gravity of 1.535 at 15° (the temperature at which all our determinations were made), but converted tribrombenzol into tribrommononitrobenzol only, when acting in the cold, although it gave the dinitro compound when boiled with it. It was therefore less efficient than our acid of specific gravity 1.51, but more so than the foreign acids mentioned above. The analyses of this acid and of our acid of 1.51 specific gravity yielded the following results, which are given in tabular form to facilitate comparison:

	Per Cent. NO₂.	Per Cent. HNO₃.	H₂O by Difference.
Acid of 1.535 sp. gr.	5.0	93.38	1.62
Acid of 1.51 sp. gr.	0.5	96.92 [1]	2.58

The nitric dioxide was determined in the usual way by treatment of the diluted acid with a standard solution of potassic permanganate. The results are not absolutely accurate, as observed by Feldhaus,[2] because of the loss of nitric dioxide in transferring the acid from the weighing or measuring tube to the beaker, but are nearly enough so for our purpose. The nitric acid was determined by neutralisation with ammonic hydrate, and weighing the ammonic nitrate dried at 120°. It contained no ammonic nitrate. The estimated amount of nitric acid corresponding to the nitric dioxide found has been subtracted, so that the number given represents the percentage of free HNO_3 in the acid. These results show that the acid with the higher specific gravity contains the smaller amount of HNO_3, and therefore that the determination of the specific gravity is not a trustworthy way of finding the strength of nitric acid, unless the sample examined is free from lower oxides of nitrogen.

[1] This number is higher than that given by Kolb as corresponding to this specific gravity (1.51), which is 94 per cent. The difference may be due to the presence of amines in the ammonia used by us; but we have not studied this point more carefully, as we are not interested in the absolute determination of the amount of HNO_3 in this acid, but only in the relative amounts of HNO_3 in these two nitric acids, which are given accurately by our numbers, since they were obtained under exactly parallel conditions.

[2] Zeitschrift für anal. Chemie **1**, 426.

After the foregoing account of our work was already written we received a paper by Nietzki and Hagenbach,[1] in which a similar experience is described ; for they found that with commercial fuming nitric acid a mononitro compound alone could be obtained from diacetylmetaphenylenediamine, whereas they obtained the dinitro compound by using " pure monohydrate," which, they say, can be prepared most easily by distilling fuming nitric acid with twice the quantity of sulphuric acid, and which had a specific gravity of 1.533 at 15°.   It is to be observed, however, that our experiment with an acid prepared in a similar way shows that even this acid is not so pure as that made direct from nitre and sulphuric acid.

Preparation of Symmetrical Trichlorbenzol.

We have tried all of the three different processes known for making trichloraniline, viz. 1st. By the direct action of chlorine on aniline dissolved in glacial acetic acid—a method which gives the trichloraniline more quickly than any of the others, but which we discarded on account of the very small yield obtained.   2d. According to Beilstein and Kurbatow,[2] by the formation of chloracetanilid from chlorine and acetanilid, and converting this, after the removal of the acetyl, into trichloraniline by treatment with chlorine in a glacial acetic acid solution.   We may be allowed to remark, in regard to this method, that we were unable to make acetanilid in glacial acetic acid solution take up more than one atom of chlorine, an excess of chlorine passing through the solution unaltered after monochloracetanilid had been formed, whereas Beilstein and Kurbatow obtained the dichloracetanilid in this way ; we have not thought the point of sufficient importance, however, to devote to it the time necessary to determine the cause of this difference.   This method gives good results, but does not lead to them so quickly and easily as the *third*, which consists in making dichloracetanilid according to Witt,[3] that is, acting on acetanilid in a warm acetic acid solution with a solution of bleaching-powder.   The dichloracetanilid was then converted into the trichloraniline, as in the second method.

The method, therefore, which we finally adopted, and should recommend as the best, is the following : 5 parts of acetanilid are

[1] Berichte der deutsch. chem. Gesell. **20,** 333.   [2] Annalen der Chemie **182,** 95.

[3] Berichte der deutsch. chem. Gesell. **8,** 1226.   Bender, ibid. **19,** 2272, has obtained C_6H_5 NClCOCH$_3$ by the action of bleaching-powder on a *cold* acetic acid solution of acetanilid.

dissolved in 20 parts of glacial acetic acid and 100 of water, and heated to boiling; then, after removing the lamp, a 10 per cent. solution of bleaching-powder is added, until a viscous precipitate is formed, the temperature being kept above 70°. The precipitate is then treated with ammonic hydrate, and crystallised from alcohol. The yield of dichloracetanilid is nearly quantitative. The dichloracetanilid is next converted into dichloraniline by heating it on the water-bath with strong sulphuric acid, the dichloraniline dissolved in glacial acetic acid, and chlorine passed through the solution until two parts of the dichloraniline have gained one part of chlorine; the product is then rendered alkaline with a large excess of sodic hydrate, and distilled with steam; the solid which distills over, after crystallisation from dilute alcohol, is pure trichloraniline, but the yield is far from satisfactory, a large quantity of tarry impurity being formed during the treatment of the free base with chlorine. The trichloraniline is converted into trichlorbenzol by the method of Bässmann;[1] that is, it is dissolved in alcohol of 95 per cent. by heat, and the calculated amount of a hot concentrated aqueous solution of potassic nitrite added, and then dilute sulphuric acid, little by little, until the reaction is strongly acid; the mixture is then warmed gently on the water-bath until the reaction comes to an end, and the trichlorbenzol purified by crystallisation from alcohol. The yield is good, 8 grams of the trichloraniline giving 5 grams of trichlorbenzol; that is, 67 per cent. of the theoretical amount.

Trichlordinitrobenzol, $C_6HCl_3(NO_2)_2$.

The symmetrical trichlorbenzol was dissolved in nitric acid[2] of specific gravity 1.505 at the ordinary temperature; the same result was also obtained if the beaker in which the reaction took place was kept cool by immersion in cold water. When the trichlorbenzol was completely dissolved, the product was precipitated by pouring it into cold water or snow, and purified by crystallisation from hot alcohol until it showed the constant melting point 129.5°, when it was dried at 100° and analysed.

0.2694 gram of the substance gave 24.4 cc. of nitrogen at 24° temperature and 766.5 mm. pressure.

[1] Annalen der Chemie **191**, 206.
[2] The nitric acid was prepared by distilling nitre with sulphuric acid in the proportions of one molecule of each. See page 350 for a discussion of this point.

0.2102 gram of substance gave, according to the method of Carius, 0.3322 gram of argentic chloride.

	Calculated for $C_6HCl_3(NO_2)_2$.	Found.
Nitrogen	10.31	10.24
Chlorine	39.22	39.07

Properties.—It forms thick, long white prisms, when crystallised from alcohol, which melt at 129.5°, and are soluble in cold alcohol, much more freely in hot, very easily soluble in benzol, chloroform, carbonic disulphide, or acetone, soluble in ether, or in glacial acetic acid, still more soluble in hot glacial acetic acid.

In order to obtain trichlormononitrobenzol, a nitric acid diluted until it shows the specific gravity 1.46 must be boiled with trichlor-benzol until complete solution takes place. After precipitation with water and recrystallisation from alcohol, the product of such a preparation showed the melting point 68°, that given by Beilstein and Kurbatow. Ordinary strong nitric acid of specific gravity 1.4 has no action on trichlorbenzol, whether hot or cold.

The constitution of the trichlordinitrobenzol follows from the fact that it is made from symmetrical trichlorbenzol, and is

$$H : Cl : NO_2 : Cl : NO_2 : Cl = 1 : 2 : 3 : 4 : 5 : 6.$$
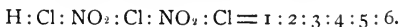
Trichlortrinitrobenzol, $C_6Cl_3(NO_2)_3$.

This substance was made by boiling in a flask, for half an hour or somewhat more, trichlordinitrobenzol with a mixture of fuming sulphuric acid and nitric acid of specific gravity 1.505, prepared direct from nitre and sulphuric acid.[1] The substance goes completely into solution while hot, but a considerable quantity separates out as it cools. The whole is then precipitated with snow, and treated with hot alcohol, when an insoluble residue containing sulphur is left behind ; this is probably a sulphone, but was formed in such small quantities that we did not try to study it. The hot alcoholic solution on cooling deposits the trichlortrinitrobenzol, which is purified by crystallisation from boiling alcohol until it shows a constant melting point 187°. The substance was dried at 100° and analysed, with the following results :

0.1656 gram of substance gave 18.8 cc. of nitrogen at a temperature of 18° and 750 mm. pressure.

[1] See page 350.

0.1486 gram of substance gave, according to the method of Carius, 0.2034 gram of argentic chloride.

	Calculated for $C_6Cl_3(NO_2)_3$.	Found.
Nitrogen	13.27	12.94
Chlorine	33.64	33.83

Properties.—The trichlortrinitrobenzol is obtained by crystallisation from alcohol in rather thick good-sized needles of a white color, with a slight yellowish tinge, melting point 187°, very nearly insoluble in water, but not completely so, less soluble in alcohol than trichlordinitrobenzol, easily soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide. Alcohol is the best solvent for it.

The constitution of the trichlortrinitrobenzol, since it is made from the symmetrical trichlorbenzol, is also symmetrical,

$$Cl : NO_2 : Cl : NO_2 : Cl : NO_2 = 1 : 2 : 3 : 4 : 5 : 6.$$
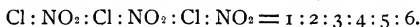
The description of the tribromtrinitrobenzol, as well as of some of the derivatives of this very reactive substance, will be postponed until another paper.

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XXIX.—ON NITRO DERIVATIVES OF OXANILIDE.

By W. G. Mixter and F. O. Walther.

Paradinitro-oxanilide.—Huebner and Rudolph[1] prepared dinitro-oxanilide by adding fuming nitric acid to a solution of oxanilide in glacial acetic acid. We have obtained the compound by treating 10 grams of oxanilide with 150 cc. of nitric acid, sp. gr. 1.4, and warming on a water-bath. The oxanilide did not dissolve, but changed to a thick pasty mass. The product was washed with water and dried at 100°. It weighed 12 grams, the theoretical yield being 13.7 grams. An estimation of nitrogen gave 17.13 per cent.; theory requires 16.97 per cent. in dinitro-oxanilide. The preparation was found to have the melting point 260°, and to yield on saponification p-nitraniline, as described by Huebner and Rudolph. The p-nitraniline obtained was found to be free from o-nitraniline.

[1] Berichte der deutsch. chem. Gesell. **8**, 473.

Tetranitro-oxanilide.—When oxanilide is slowly added to red fuming nitric acid it dissolves, and after a few minutes small crystals appear. On warming, crystals form abundantly. To complete the reaction we usually boiled the solution ten to fifteen minutes. After cooling, the crystalline mass was filtered on a perforated platinum cone, washed two or three times with nitric acid, sp. gr. 1.4, then with water and, finally, once with alcohol, and dried at 100°. 10 grams of oxanilide yielded 11 grams, and sometimes a little more, of crystals of tetranitro-oxanilide. The acid filtrate from the crystals, on diluting with water, gave a precipitate of tetranitro-oxanilide, rather less than half the weight of the crystalline portion and not quite as pure. The following analyses are of two different preparations:

I. 0.5297 gram gave 0.7711 gram CO_2 and 0.0981 gram H_2O. 0 4247 gram gave 72.75 cc. N at 21° and 768.4 mm.

II. 0.4982 gram gave 0.7211 gram CO_2 and 0.0854 gram H_2O. 0.4406 gram gave 74.2 cc. N at 14° and 759 mm.

	Theory.	I.	II.
C_{14}	40.00	39.69	39.92
H_8	1.90	2.06	1.91
N_6	20.00	20.20	20.12
O_{10}	38.10	...	...
	100.00		

Tetranitro-oxanilide has a white color, melts at 300°, is but slightly soluble in hot alcohol and benzene and glacial acetic acid. It is readily saponified by a hot two per cent. potassium hydroxide solution, by warm oil of vitriol, and by an alcoholic ammonia solution at 100°, yielding 1 : 2 : 4 dinitroaniline, melting at 182°.

It has, therefore, the constitution represented by

$$CO\overset{1}{N}HC_6H_3\overset{2}{N}O_2\overset{4}{N}O_2$$
$$\underset{1}{C}ONHC_6\underset{2}{H}_2NO_2\underset{4}{N}O_2.$$
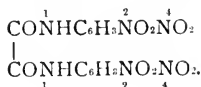
Hexnitro-oxanilide.—Oxanilide, 10 grams, was dissolved in 150 cc. of red fuming nitric acid at ordinary temperature, and oil of vitriol, 150 cc., was added. A bulky precipitate, consisting of minute pearly scales, at once separated. After warming for half an hour on a water-bath the mixture was cooled, poured into cold water, and the precipitate was filtered and thoroughly washed with

water. The product, dried at 100°, weighed 19.3 grams. It is designated as A. Another preparation, B, was made as above described, only in place of oil of vitriol, warm fuming sulphuric acid was used, and the acid mass was poured into snow. The yield was 20.7 grams. Another time the fuming sulphuric acid was heated to 100° before adding it to the nitric acid solution, and no higher nitro compound was obtained. The yield was less than in the preparations A and B.

Analysis of A.—0.4272 gram gave 0.5225 gram CO_2 and 0.0506 gram H_2O.

0.3789 gram gave 64.7 cc. N at 4° and 768.7 mm.

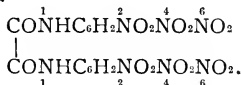Analysis of B.—0.5794 gram gave 0.700 gram CO_2 and 0.0662 gram H_2O.

0.3700 gram gave 67.6 cc. N at 13° and 765.5 mm.

	Theory.	A.	B.
C_{14}	32.94	33.33	32.95
H_6	1.18	1.32	1.23
N_8	21.96	21.38	22.03
O_{14}	43.92	...	...
	100.00		

Hexnitro-oxanilide melts at 300°, has a white pearly lustre, is slightly soluble in boiling alcohol and benzene, and is somewhat more soluble in hot glacial acetic acid.

It does not dissolve in oil of vitriol at 100°, but complete solution results on raising the temperature to 200°, and trinitraniline is formed. That which we obtained after recrystallising once from alcohol melted at 188°, the melting point of the only trinitraniline known in which $NH_2 : NO_2 : NO_2 : NO_2 = 1 : 2 : 4 : 6$.

An estimation of nitrogen gave 24.73 per cent.; theory requires 24.56 per cent. in $C_6H_2(NO_2)_3NH_2$. The hexnitro-oxanilide therefore has the formula

$$\overset{1}{C}ONHC_6H_2\overset{2}{N}O_2\overset{4}{N}O_2\overset{6}{N}O_2$$
$$\underset{1}{C}ONHC_6H_2\underset{2}{N}O_2\underset{4}{N}O_2\underset{6}{N}O_2.$$

Hexnitro-oxanilide differs from the other oxanilides in its deportment towards alkalies. It dissolves quickly in hot alkaline solutions, forming a deep red solution of two or more compounds. In one experiment 2 grams of hexnitro-oxanilide were treated with

5 grams of potassium hydroxide in 100 cc. of water.   The solution was boiled for two hours ; ammonia was given off. To the solution acetic acid was added in excess, and the small black precipitate which formed was filtered and dissolved in hot water.   Nothing separated on cooling this last solution.   We then tried the action of ammonia as follows : 5 grams of hexnitro-oxanilide were placed in a litre of boiling water containing a little ammonia; the red solution was filtered from a yellow insoluble part, doubtless trinitraniline.   The solution on cooling yielded brilliant small crystals of a red color, showing also golden tints.   Two different preparations of these crystals dried at 100° gave the following results on analysis :

Carbon	32.18	32.53
Hydrogen	2.41	2.39
Nitrogen	24.92	24.87

These figures do not correspond to any simple atomic ratio and we do not understand what compounds composed the mixture, except that subsequent results indicate that an ammonium salt of trinitrophenyloxamide was present.   The red crystals were next dissolved in water, and acetic acid in one case, and hydrochloric acid in another, added.   A light yellow precipitate slowly separated on boiling, which was washed, dried, and gave analytical results which indicated a mixture.   In another experiment 10 grams of hexnitro-oxanilide were treated with a litre of boiling water containing 100 cc. of concentrated ammonia.   The insoluble portion was found to be trinitraniline.   The filtered solution was acidified with hydrochloric acid.   The red color slowly disappeared. The precipitate was washed with *cold* water and dissolved in boiling glacial acetic acid.   The solution on cooling changed to a jelly.   The acetic acid was removed by repeated evaporations with alcohol, and finally a fibrous mass was obtained, which was washed with alcohol and dried.   It is designated as A.   Next 10 grams of hexnitro-oxanilide were placed in 300 cc. of boiling water in which 30 grams of hydrogen potassium carbonate had been dissolved; carbon dioxide was set free by the anilide, and the escaping steam gave a faint reaction for ammonia.   Only a small residue remained undissolved.   The solution on slow cooling deposited red crystals of a potassium salt, or salts in appearance like those obtained with ammonia.   They were filtered and washed

moderately with *cold* water. The filtrate from the crystals was acidified, the slight precipitate which formed was removed, and this solution was evaporated to dryness. The residue was treated with cold water, the solution filtered, made acid with acetic acid, and calcium chloride added. The calcium salt obtained was analysed and found to be oxalate, thus proving that oxalic acid is one of the products of the decomposition of hexnitro-oxanilide by potassium carbonate. The red crystals of the potassium salt above mentioned were placed in about 250 cc. of water, and acetic acid in large excess was added. The whole was boiled until the red color disappeared, and the yellow product was filtered and washed with *cold* water. The product was treated with about 800 cc. of boiling alcohol, which dissolved most of it. The alcoholic solution on cooling and evaporating spontaneously yielded a fibrous mass, which was filtered, washed with cold alcohol, and dried at 100°. It weighed 2.3 grams, and is designated as B.

In the next experiment 27 grams of hexnitro-oxanilide and an equal weight of hydrogen potassium carbonate and about 800 cc. of water were used. The insoluble portion which remained on boiling was removed; it proved to be trinitraniline. The potassium salt which separated on cooling the solution was filtered, the filtrate was made acid with acetic acid, heated to boiling, and the slight precipitate which formed was removed. This solution on cooling deposited potassium picrate, from which picric acid was obtained, as was proved by its melting point, 122°, and its reactions with potassium cyanide and with ammoniacal copper sulphate. The potassium salt obtained, not the picrate, was dissolved in hot water and decomposed by acetic acid. The precipitate was treated several times with hot water, but only for a short time. It is designated as C.

Analysis of A.—0.4644 gram gave 0.5456 gram CO_2 and 0.0753 gram H_2O.

0.4251 gram gave 84.6 cc. N at 11° and 742 mm.

Analysis of B.—0.4723 gram gave 0.5557 gram CO_2 and 0.0753 gram H_2O.

0.4126 gram gave 77.14 cc. N at 4.7° and 768 mm.

Analysis of C.—0.502 gram gave 0.5866 gram CO_2 and 0.0787 gram H_2O.

0.4474 gram gave 84.2 cc. N at 9° and 763 mm.

26

	Calculated for	A.	B.	C.
C_8	32.11	32.04	32.09	31.69
H_5	1.67	1.78	1.77	1.74
N_5	23 41	23.46	23.33	22.98
O_8	42.81	...	...	...
	100.00			

The results show that the substance purified by three different methods has the formula $C_8H_5N_5O_8$.

The substance was warmed with sulphuric acid, and in the escaping gases carbon monoxide and dioxide were identified, and from the acid solution trinitraniline was separated. The potassium salt, described later, was found to decompose slowly when its aqueous solution was boiled, with formation of trinitraniline and oxalic acid. These reactions indicate that the substance is trinitrophenyl-oxamide, having the formula
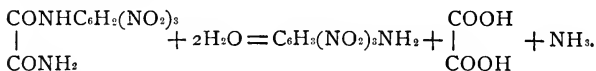
$$CONHC_6H_2(NO_2)_3$$
$$|$$
$$CONH_2.$$
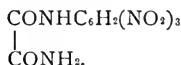
Trinitrophenyl-oxamide melts with decomposition at $255°$–$260°$. It is slightly soluble in alcohol, but dissolves readily in hot glacial acetic acid, from which it separates on cooling in white fibres. Its potassium salt, made in and crystallised from hot alcohol, was found to contain 11.64 per cent. of potassium ; theory requires 11.57 per cent. in $C_8H_4N_5O_8K$. A preparation of potassium salt which was crystallised from hot water yielded only 10.31 per cent. of potassium, and in crystals obtained from hexnitro-oxanilide and potassium carbonate only 9.96 per cent. of potassium was found. These two results are due to the decomposition already mentioned of the potassium salt. Trinitrophenyl-oxamide forms compounds with zinc, calcium, barium, and silver, which have not been analysed. The ammonium salt forms brilliant yellowish-red thin crystals, like the potassium salt in appearance. Both explode violently on heating. The strong acidic character of trinitrophenyl-oxamide is indicated by the fact that solutions of its ammonium and potassium compounds are not decomposed, or only partly, by hydrochloric and acetic acids at ordinary temperature.

The decomposition of hexnitro-oxanilide by potassium carbonate or ammonia is evidently as follows :

$$\begin{array}{c} \text{CONHC}_6\text{H}_2(\text{NO}_2)_3 \\ | \\ \text{CONHC}_6\text{H}_2(\text{NO}_2)_3 \end{array} + \text{H}_2\text{O} = \begin{array}{c} \text{CONHC}_6\text{H}_2(\text{NO}_2)_3 \\ | \\ \text{CONH}_2 \end{array} + \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}.$$

At the same time the trinitrophenyl-oxamide is partly converted into trinitraniline and oxalic acid, thus:

$$\begin{array}{c} \text{CONHC}_6\text{H}_2(\text{NO}_2)_3 \\ | \\ \text{CONH}_2 \end{array} + 2\text{H}_2\text{O} = \text{C}_6\text{H}_2(\text{NO}_2)_3\text{NH}_2 + \begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} + \text{NH}_3.$$

Water is represented as taking part in the reactions to avoid formulating the compound of trinitrophenyl-oxamide with potassium, whose constitution has not been determined. It should be stated that di- and tetranitro-oxanilide do not yield analogues of trinitrophenyl-oxamide, and that from none of the nitro-oxanilides have oxanilic acids been obtained.

XXX.—ON NITRO DERIVATIVES OF DIBROM-OXANILIDE.

By W. G. Mixter and C. P. Willcox.

Dinitrodibrom-oxanilide.—Paradibrom-oxanilide, 5 grams, and nitric acid, sp. gr. 1.4, 150 cc., were boiled gently for half an hour. The dibromoxanilide only partly dissolved. After cooling, the whole was poured into cold water, and the insoluble portion was filtered, washed thoroughly with water and once with alcohol, and dried at 100°. The following is the analysis:

I. 0.5252 gram gave 0.676 gram CO_2 and 0.0823 gram H_2O.
II. 0.7495 gram gave 0.959 gram CO_2 and 0.1173 gram H_2O.
III. 0.3128 gram gave 0.4013 gram CO_2.
IV. 0.4337 gram gave 41 cc. N at 4° and 748.8 mm.
V. 0.4088 gram gave 0.3147 gram AgBr.

	Theory.	I.	II.	III.	IV.	V.
C_{14}	34.42	35.09	34.89	34.98	...	...
H_8	1.64	1.74	1.74	...	...	...
N_4	11.47	...	...	...	11.53	...
Br_2	32.79	...	...	...	...	32.75
O_6	19.68	...	...	...	...	...
	100.00					

Dinitrodibrom-oxanilide has a yellow color, melts at 285° to 288°, is insoluble in boiling alcohol and benzene, and is soluble in hot aniline. It was saponified by potassium hydroxide solution, and the nitrobromaniline obtained melted at 107°. Another portion was saponified with warm oil of vitriol, and the resulting nitrobromaniline after recrystallising from hot water melted at 110°.

The melting point of o-nitro-p-bromaniline is 111.4°, hence the dinitrodibrom-oxanilide has the formula

$$CONHC_6H_3\overset{2}{N}O_2\overset{4}{Br}$$
$$\underset{1}{|}$$
$$CONHC_6H_2NO_2Br.$$
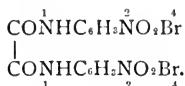
It should be mentioned that in one experiment we failed to obtain nitration of all the bromoxanilide, but from the mixture prepared o-nitro-p-bromaniline.

Tetranitrodibrom-oxanilide.—In attempting to introduce more than two nitro groups into dibromoxanilide we have found it difficult to obtain pure products. In one experiment 5 grams of dibromoxanilide were added gradually to 150 cc. of fuming nitric acid. The mixture was stirred frequently, and after half an hour was poured into snow. The substance was analysed, but a formula could not be deduced from the results. In another trial dibrom-oxanilide was added to fuming nitric acid, cooled by a freezing mixture, and the nitrogen found in the product was only 12.9 per cent. When dibromoxanilide is dissolved in warm red fuming nitric acid, bromine is set free. The solution, when concentrated by boiling, deposits crystals. We used 20 cc. of fuming acid for every gram of dibromoxanilide taken. The crystals were washed first with nitric acid of 1.4 sp. gr. and then with water, and analysed with the following results:

I.   0.3368 gram gave 0.3552 gram CO_2 and 0.0331 gram H_2O.
II. 0.2470 gram gave 0.2623 gram CO_2 and 0.0253 gram H_2O.
III. 0.5555 gram gave 65.56 cc. N at 7.6° and 768.1 mm.
IV. 0.3545 gram gave 41.21 cc. N at 4.7° and 772.3 mm.
V.   0.6016 gram gave 0.392 gram AgBr.

The theory given is for
$$CONHC_6H_2(NO_2)_2Br$$
$$|$$
$$CONHC_6H_2(NO_2)_2Br.$$

	Theory.	I.	II.	III.	IV.	V.
C_{14}	29.06	28.76	28.96	...	...	...
H_6	1.04	1.09	1.13	...	...	...
N_6	14.53	...	...	14.58	14.59	...
Br_2	27.68	...	...	...	...	27.72
O_{10}	27.69	...	...	...	...	...

Tetranitrodibrom-oxanilide forms white needles which melt at 285°–287°. It is almost insoluble in boiling alcohol, and is sparingly soluble in boiling glacial acetic acid, from which it separates on cooling in white fibres. We have not succeeded in obtaining dinitrobromaniline by saponifying the substance with sulphuric acid, in which it dissolves on heating, or with potassium hydroxide.

As hexnitro-oxanilide behaves differently from other oxanilides when treated with alkalies (see preceding article), we have endeavored to obtain a similar decomposition of tetranitrodibrom-oxanilide, but as yet have no results, owing to lack of material and time. Its solution in hot alcoholic ammonia deposited on cooling a yellow mass, which, after drying, melted at 285°. The tetranitrodibrom-oxanilide was found to dissolve in hot aqueous alcohol containing potassium carbonate. Nothing separated from the solution on cooling.

The filtrate from the crystals of tetranitrodibrom-oxanilide which separated from nitric acid in the preparation, yielded a nearly white precipitate on diluting with water. It was washed with water and dried at 100°. It is designated as A, and another preparation obtained in the same way as B.

Analysis of A.—I. 0.4045 gram gave 0.4958 gram CO_2 and 0.0538 gram H_2O.

II. 0.3945 gram gave 55.2 cc. N at 8.2° and 739.4 mm.

III. 0.2407 gram gave 0.0993 gram AgBr.

Analysis of B.—IV. 0.4256 gram gave 0.515 gram CO_2 and 0.0578 gram H_2O.

V. 0.4095 gram gave 53.12 cc. N at 4° and 772 mm.

VI. 0.4522 gram gave 0.191 gram AgBr.

	Theory.	I.	II.	III.	IV.	V.	VI.
C_{12}	33.64	33.42	...	...	33.00	...	...
H_6	1.40	1.48	...	...	1.48	...	...
N_5	16.35	...	16.59	...	...	16.25	...
Br	18.69	...	...	17.55	...	...	18.49
O_8	29.92	...	...	...	...	...	...
	100.00						

The results correspond fairly well with the calculated formula. The constitution of the substance has not been made out. It is soluble in dilute ammonia, and the solution yields a barium salt on addition of a solution of barium chloride.

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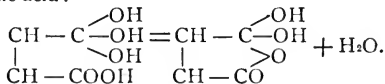# REMARKS ON THE CONSTITUTION OF LEVULINIC AND MALEIC ACIDS.

By Arthur Michael.

Several years ago, W. Roser[1] attempted to explain the isomerism of maleic and fumaric acids by assuming the first-named substance to be an anhydride of a hypothetical orthomaleic acid. At the time of its publication this view was without an experimental basis ; but R. Anschütz,[2] in recently reviving it, has endeavored to prove that subsequent discoveries have given this hypothesis the needed experimental support. The constitution of maleic and fumaric acids is one of the most important problems of organic chemistry, and I therefore deemed an examination of Roser's hypothesis of interest, particularly as Anschütz's paper may seem to establish this view with some certainty.

According to Roser, maleic and fumaric acids are expressed by the following constitutions :

$$
\begin{array}{ll}
\begin{array}{l}
\quad\quad\quad\diagup \mathrm{OH} \\
\mathrm{CH} - \mathrm{C} \hspace{-0.3em}-\hspace{-0.3em}\mathrm{OH} \\
| \quad\quad\diagup \mathrm{O} \\
\mathrm{CH} - \mathrm{CO},
\end{array}
&
\begin{array}{l}
\mathrm{CH} - \mathrm{COOH} \\
| \\
\mathrm{CH} - \mathrm{COOH}.
\end{array}
\end{array}
$$

Maleic acid is therefore the anhydride of an acetyleneorthodicarboxylic acid :

$$
\begin{array}{l}
\quad\quad\quad\diagup\mathrm{OH} \quad\quad\quad\quad\quad\diagup\mathrm{OH} \\
\mathrm{CH} - \mathrm{C}\hspace{-0.3em}-\hspace{-0.3em}\mathrm{OH} = \mathrm{CH} - \mathrm{C}\hspace{-0.3em}-\hspace{-0.3em}\mathrm{OH} \\
| \quad\quad\nwarrow\mathrm{OH} \quad | \quad\quad\diagup\mathrm{O} \quad + \mathrm{H_2O}. \\
\mathrm{CH} - \mathrm{COOH} \quad\quad \mathrm{CH} - \mathrm{CO}
\end{array}
$$

This conception of the constitution of maleic acid rests on two assumptions, which are, that the acid contains a typical carbon with a strong affinity for two hydroxyls, and that carboxyl and ortho-

[1] Berichte der deutsch. chem. Gesell. **14**, 2546.

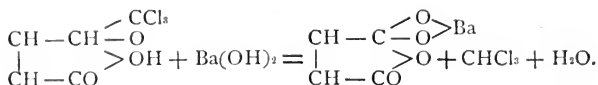[2] This Journal **9**, 253; Annalen der Chemie **239**, 161.

carboxyl in the γ-position are unstable, and undergo a spontaneous decomposition under elimination of water. Anschütz explains the first assumption by calling attention to the existence of chloralhydrate, mesoxalic and dioxytartaric acids, which compounds, like Roser's constitution of maleic acid, contain a carbon that is in union with strong negative groups. Acetic aldehyde does not form a hydrate with water, but the replacement of the methyl-hydrogen by halogen gives rise to compounds possessing that property. It evidently follows that the replacement of hydrocarbon-hydrogen in maleic and similar acids by halogens should strengthen the affinity of the two hydroxyls to the typical carbon, and the halogen acids should therefore be more stable towards heat than the original compounds. It is worthy of note, however, that the introduction of halogen has exactly the contrary effect. While maleic and citraconic acids are perfectly stable even at 100°, dibrommaleic and monobromcitraconic acids decompose, more or less completely, at ordinary temperature into anhydrides and water.

In considering the facts adduced by Anschütz in support of Roser's maleic acid constitution, their order, as given in his paper, will be followed. One of Anschütz's principal proofs is found in the discovery of Bredt,[1] that levulinic acid heated with acetic anhydride gives an acetyl derivative. Although Bredt states that this fact is not in accordance with the generally adopted constitution of the acid, he also calls attention to the behavior of the acid towards hydroxylamine, phenylhydrazine, and hydrocyanic acid, as proving the presence of carbonyl in levulinic acid, and that these reactions are in harmony with the old constitution and not with the one he suggests :

$$
\begin{array}{ll}
\text{CH}_2\text{— CO — CH}_3 & \text{CH}_2\text{— C} \overset{\diagup \text{CH}_3}{\underset{\diagdown \text{O}}{\text{— OH}}} \\
\mid & \mid \\
\text{CH}_2\text{— COOH,} & \text{CH}_2\text{— CO.} \\
\quad\text{Old constitution.} & \quad\text{New constitution.}
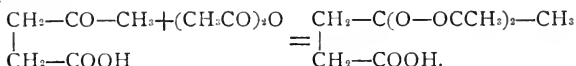\end{array}
$$
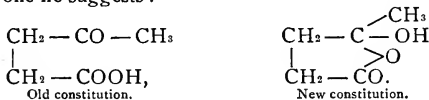
Anschütz, however, believes that the formation of an acetyl derivative proves the new constitution beyond a doubt, and changes the constitutions of a number of analogous substances in a corresponding manner. Accordingly, the constitution of trichlorphenomalic acid is changed to contain an anhydro-oxygen, and its conversion by barium hydrate into maleic acid is considered as proving Roser's view in regard to the constitution of that acid :

[1] Annalen der Chemie **236**, 225.

$$\begin{array}{l} CH-CH \overset{\diagup CCl_3}{\underset{\diagdown O}{-O}} \\ | \qquad\qquad >OH + Ba(OH)_2 = \\ CH-CO \end{array} \quad \begin{array}{l} CH-C \overset{\diagup O}{\underset{\diagdown O}{\diagup}} Ba \\ | \qquad\qquad >O + CHCl_3 + H_2O. \\ CH-CO \end{array}$$
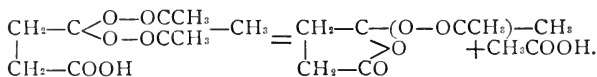
It seems to me that the formation of the so-called acetyl-levulinic acid is a result of the relative positions of carbonyl and carboxyl in the old constitution of the acid, and that, when this relation is duly considered, it will be found that the formation of the acetyl compound is simply what should be expected.

It is a well-known fact that aldehydes unite with acid anhydrides and chlorides to form ethers. Although, to my knowledge, this reaction has not been realised with ketones, no one bearing the close similarity in the reactions of aldehydes and ketones in mind can well doubt that ketones are capable of forming similar compounds. We may therefore suppose that the first phase in the action of acetic anhydride on levulinic acid is to form a diacetyl product:

$$\begin{array}{l} CH_2-CO-CH_3 + (CH_3CO)_2O \\ | \\ CH_2-COOH \end{array} = \begin{array}{l} CH_2-C(O-OCCH_3)_2-CH_3 \\ | \\ CH_2-COOH. \end{array}$$

This compound is the acetyl derivative of a γ-dihydroxyvaleric acid, and we know that hydroxyl and, probably still more readily, the group $-O-OCCH_3$ in the γ- and δ-positions to carboxyl, have a tendency to undergo a condensation.[1] The second phase of the reaction therefore consists in the elimination of acetic acid, and is represented as follows:

$$\begin{array}{l} CH_2-C \overset{\diagup O-OCCH_3}{\underset{\diagdown O-OCCH_3}{\diagup}} -CH_3 \\ | \\ CH_2-COOH \end{array} = \begin{array}{l} CH_2-C-(O-OCCH_3)-CH_3 \\ | \qquad\qquad >O \\ CH_2-CO \end{array} + CH_3COOH.$$

It will be noticed that the constitution of the acetyl derivative is identical, no matter which of the two structural formulæ of levulinic acid is used, and that the new interpretation of its formation is in complete accordance with the old carbonyl-constitution of the acid. While the old constitution explains in a satisfactory manner the formation of levulinic acid from acetylsuccinic ether and all its reactions, the new constitution suggested by Bredt, and adopted by Anschütz, cannot be brought in harmony with that synthesis

[1] Tiemann and Herzfeld (Berichte der deutsch. chem. Gesell. **10**. 287) have shown that coumarine is readily formed when acetylcoumaric acid is heated, but cannot be obtained by heating coumaric acid.
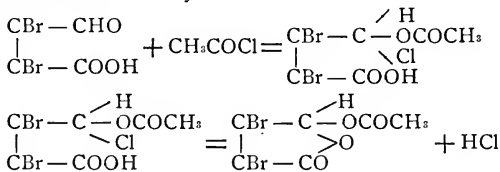
nor with its principal reactions. I do not hesitate to assert that the old constitution of levulinic acid has been established with a certainty that is uncommon among carbon derivatives of the higher series. If, as Anschütz[1] asserts, Kekulé and Strecker[2] have proved that trichlorphenomalic acid is an "unsaturated levulinic acid in which the hydrogen of the methyl has been replaced by chlorine," then it is evident that its decomposition by barium hydrate into maleic acid and chloroform speaks with as much force against Roser's constitution as Anschütz supposed the reaction to speak in its favor :

$$
\begin{array}{l}
\text{CH—CO—CCl}_3 + \text{Ba(OH)}_2 \\
| \\
\text{CH—COOH}
\end{array}
=
\begin{array}{l}
\text{CH—COO} \\
| \qquad\qquad >\text{Ba} + \text{CHCl}_3 + \text{H}_2\text{O} \\
\text{CH—COO}
\end{array}
$$
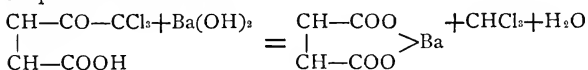
The explanation of the formation of acetyl-levulinic acid given above applies equally to that of the so-called acetylmucobromic acid. Jackson and Hill[3] have shown that mucobromic acid and acetyl chloride heated at 120° give an acetyl derivative, and Anschütz considers its formation as proving the following constitutions :

$$
\begin{array}{ll}
\begin{array}{l}
\quad\quad\; \diagup \text{H} \\
\text{CBr—C} \overset{}{\underset{}{}} \text{OH} \\
| \qquad\;\; >\text{O} \\
\text{CBr—CO}
\end{array}
&
\begin{array}{l}
\quad\quad\; \diagup \text{H} \\
\text{CBr—C} \overset{}{\underset{}{}} \text{OCOCH}_3 \\
| \qquad\;\; >\text{O} \\
\text{CBr—CO}
\end{array} \\
\text{Mucobromic Acid.} & \text{Acetylmucobromic Acid.}
\end{array}
$$
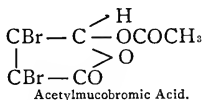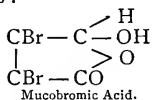
From the new point of view, the formation of the so-called acetylmucobromic acid is a result of the property of aldehydes to unite with acid chlorides, and the presence of a reactive chlorine, due to the juxtaposition of the negative group OCOCH_3, in the γ-position towards carboxyl :

$$
\begin{array}{l}
\text{CBr—CHO} \\
| \qquad\qquad + \text{CH}_3\text{COCl} = \\
\text{CBr—COOH}
\end{array}
\begin{array}{l}
\quad\quad\; \diagup \text{H} \\
\text{CBr—C} \overset{}{\underset{}{}} \text{OCOCH}_3 \\
| \qquad\;\; \diagdown \text{Cl} \\
\text{CBr—COOH}
\end{array}
$$

$$
\begin{array}{l}
\quad\quad\; \diagup \text{H} \\
\text{CBr—C} \overset{}{\underset{}{}} \text{OCOCH}_3 \\
| \qquad\;\; \diagdown \text{Cl} \\
\text{CBr—COOH}
\end{array}
=
\begin{array}{l}
\quad\quad\; \diagup \text{H} \\
\text{CBr—C} \overset{}{\underset{}{}} \text{OCOCH}_3 \\
| \qquad\;\; >\text{O} \\
\text{CBr—CO}
\end{array}
+ \text{HCl}
$$

The anil of maleic acid treated with alkalies gives a salt of fumaric acid and aniline. This interesting fact has been used by Anschütz to corroborate Roser's hypothesis of the constitution of

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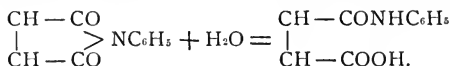[1] This Journal **9**, 263 ; Annalen der Chemie **239**, 176.   [2] Ibid. **223**, 170.
[3] This Journal **3**, 42.

maleic acid. According to this interpretation, the anil assimilates water to pass over into the acid anilide of fumaric acid, a reaction that Anschütz represents as follows:

$$
\begin{matrix}
CH-CO \\
| \qquad > NC_6H_5 + H_2O = \\
CH-CO
\end{matrix}
\qquad
\begin{matrix}
CH-CONHC_6H_5 \\
| \\
CH-COOH.
\end{matrix}
$$
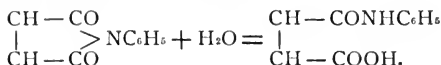
It has already been stated that Roser's hypothesis necessitates assuming a carbonyl in maleic anhydride with a strong affinity for water, and a typical carbon in the acid with an affinity for two hydroxyls. If the so-called anil of maleic acid is, as Anschütz supposes, a derivative of maleic acid, it should behave towards alkalies exactly as maleic anhydride does; that is, its carbonyl should assimilate water to form an acid anilide of maleic acid:

$$
\begin{matrix}
CH-CO \\
| \qquad > NC_6H_5 + H_2O = \\
CH-CO
\end{matrix}
\qquad
\begin{matrix}
CH-CONHC_6H_5 \\
| \\
CH-COOH.
\end{matrix}
$$

When experiments show, however, that the acid anilide of fumaric acid is the compound formed in this reaction, we are forced to the conclusion that the affinity of carbonyl for water, which is so characteristic for maleic anhydride, has been lessened by the replacement of oxygen by NC_6H_5, although that radical is obviously of a pronounced negative character. If we accept this second, in itself improbable, assumption, it is evident that the change from a maleic to a fumaric derivative consisted not in the mere mechanical rearrangement of formulæ as represented by Anschütz, but in the replacement of oxygen by NC_6H_5; hence the so-called maleinanil is, properly speaking, the anil of fumaric acid, and its decomposition into that acid is simply what might be expected. But the assumption that the replacement of an oxygen in maleic anhydride by NC_6H_5 lessens the affinity of carbonyl for water is directly contradicted by the behavior of citraconanil with alkalies. According to Gottlieb,[1] citraconanil, or methylmaleinanil, heated for a short time with dilute ammonia gave ammonium citraconate and aniline. As the replacement of hydrocarbon-hydrogen by alkyl in the acids of the maleic series increases the tendency of these compounds to form anhydrides, or, in other words, lessens the affinity of the typical carbon for hydroxyl, we should expect, if the second assumption is valid, that the replacement of an oxygen in citraconic or methylmaleic anhydride by

[1] Annalen der Chemie **77**, 28.

NC_6H_5 would give, even more readily than the corresponding change in maleic anhydride gives fumaranil, mesacon-, or methyl-fumaranil. The formation of citraconic acid from citraconanil is a decisive proof that the second assumption is inadmissible, and the formation of fumaric acid for the so-called maleinanil is there-fore a fact that cannot be explained by Roser's hypothesis.

According to Anschütz, the monobrom-substitution and brom-addition-products of maleic and fumaric acids are represented by the following constitutions:

$$CBr — COOH$$
$$|$$
$$CH — COOH$$
Bromfumaric Acid.

$$CBr — C = (OH)_2$$
$$| \quad > O$$
$$CH — CO$$
Brommaleic Acid.

$$CHBr — COOH$$
$$|$$
$$CHBr — COOH$$
Ordinary Dibromsuccinic Acid.

$$CHBr — C = (OH)_2$$
$$| \quad > O$$
$$CHBr — CO$$
Isodibromsuccinic Acid.
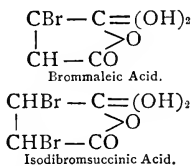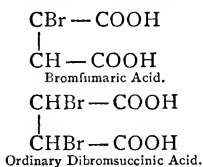
If we accept these structural formulæ, which are a logical sequence of Roser's hypothesis, it is evident that ordinary dibrom-succinic acid on losing bromhydric acid should give bromfumaric acid, and from isodibromsuccinic acid brommaleic acid should be obtained. The experimental results of these reactions are quite the reverse, as it has been found that ordinary dibromsuccinic acid yields brommaleic acid, and isodibromsuccinic gives bromfumaric acid. It may be suggested that at least the latter of these reactions can be explained by assuming brommaleic acid to be the primary product, and that this is converted into bromfumaric acid by the bromhydric acid formed in the reaction. The conversion of brom-maleic into bromfumaric acid by extremely dilute bromhydric acid has never been observed; and, moreover, even this explanation cannot be upheld, as the neutral salts of isodibromsuccinic acid also give bromfumaric acid, and the presence of free bromhydric acid under these conditions can scarcely be assumed.[1] These reactions are, in my opinion, altogether incompatible with Roser's hypothesis, and they indicate that the introconversion of maleic and fumaric derivatives is accompanied by some change in the acetylene radical. Racemic acid, according to Anschütz, contains two carboxyls, while inactive tartaric acid is a so-called dioxylactone compound. We may therefore expect that the replacement of

[1] Mesadibrompyrotartaric acid boiled with water should give, according to Anschütz, brom-mesaconic acid, but bromcitraconic acid is really formed in the reaction.

bromine in ordinary dibromsuccinic acid by hydroxyl should give exclusively racemic acid, but in fact a mixture of inactive tartaric and racemic acids is formed. On the other hand, isodibromsuccinic acid should yield in the same reaction inactive tartaric acid, but in reality it gives racemic acid.

Anschütz has stated his inability to explain the conversion of maleic into fumaric ether by traces of iodine, and the behavior of the first-named ether towards bromine vapor undoubtedly presents the same difficulty, although he makes no mention of this reaction in his paper. It seems almost impossible to rationally connect the conversion of maleic into fumaric ether by contact with bromine vapor, with Roser's formulæ for these compounds.

The second assumption on which Roser's constitution of maleic acid rests is that carbonyl and orthocarbonyl [$C(OH)_3$] in the γ-position are unstable, they undergoing a condensation to form an anhydride. This assumption follows from the behavior of lactones towards bases, when they take up water to form salts of oxy-acids, and the replacement of the γ-hydrogen of a lactone by negative hydroxyl can possibly have no other effect than to greatly facilitate the property of assimilating water by such compounds. It is evident that a compound like Roser's constitution of maleic acid heated with an excess of alkali must assimilate water and form a salt of mono-orthomaleic acid, but as maleic acid can be boiled with strong alkalies, and obtained unchanged by addition of mineral acids to this solution, we must, to explain this fact, assume that the free ortho-acid decomposes spontaneously into water and maleic acid. Anschütz explains the conversion of maleic into fumaric acid by mineral acids by supposing an addition and subsequent elimination of the mineral acid:

$$\begin{array}{l} CH-\overset{\displaystyle\nearrow OH}{\underset{\displaystyle\searrow Cl}{C}-OH} \\ | \\ CH-COOH \end{array} = \begin{array}{l} CH-COOH \\ | \\ CH-COOH \end{array} + HCl.$$
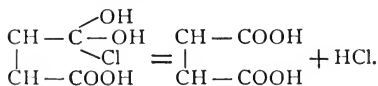
This explanation appears to me to be in conflict with the original hypothesis. If mono-orthomaleic acid eliminates water from hydroxyls in the γ-position, the monochloride of such a compound should decompose into chlorhydric and maleic acids with still greater facility, as the replacement of one of the hydroxyls of succinic and similar acids by chlorine forms monochlorides that decompose spontaneously into anhydrides and chlorhydric acid. The

replacement therefore of a hydroxyl of mono-orthomaleic acid by the more negative chlorine could only have the effect of making the maleic character of the compound more pronounced. This contradiction becomes even more apparent in considering the conversion of maleic into fumaric acid by dilute nitric acid. Anschütz would have to explain this conversion by assuming an addition and subsequent subtraction of nitric acid in a manner similar to that already assumed with chlorhydric acid. Dilute nitric acid consists of a mixture of a strong negative compound, nitric acid, and a substance, water, that in comparison acts as a base ; and it is evident that the negative anhydride of orthomaleic acid should unite with the base and not with the negative component of the mixture. If Anschütz's explanation were correct, boiling water should convert maleic much more readily into fumaric acid than dilute nitric acid does, although in fact it is without action on the acid.

The capability of compounds like Roser's maleic ether existing can hardly be doubted, and such a substance has probably been obtained by Graebe [1] by the action of tetrachlorphthalylchloride on sodium ethyl oxide, but the reactions and introconvertibility of maleic and fumaric derivatives cannot be brought in harmony with the assumption that maleic ether belongs to that group. In fact, the formation of unsymmetrical tetrachlorphthalic ether in itself contradicts Roser's views. According to his hypothesis, tetra-

chlorphthalic acid should have the constitution $C_6Cl_4\!\!\begin{array}{c}C(OH)_2\\>O\\CO\end{array}$

and the ether obtained by the action of ethyl iodide on the silver salt of such an acid should therefore be identical with the ether obtained from the chloride and sodium ethyl oxide, while in fact two isomeric ethers were obtained. It would be no rash prediction that Graebe's unsymmetrical ether will pass over into the symmetrical form on heating, as the instability of similar unsymmetrical ethers has already been observed in ortho-compounds like

$C_6H_4\!\!\begin{array}{c}N(CH_3)_3\\>O\\CO\end{array}$ and $C_6H_4\!\!\begin{array}{c}N(CH_3)_3,\\|\\O\end{array}$ which on heating are con-

verted into $C_6H_4\,\dfrac{N(CH_3)_2}{COOCH_3}$ and $C_6H_4\,\dfrac{N(CH_3)_2}{OCH_3}$; and further, that

[1] Berichte der deutsch. chem. Gesell. **16**, 860.

an acid corresponding to such unsymmetrical ethers would, if capable of existing, be extremely unstable.

In the preceding remarks, Roser's hypothesis on the constitution of maleic derivatives has been analysed for the first time, and it has been shown that while some of the reactions are incompatible with the hypothesis, others can be explained only by making a second assumption to explain the first; but a closer examination showed that these two assumptions are in themselves contradictory. These explanations are based solely on mechanical formula-twisting; a method of explaining that appeals more to the eye than to the mind, and will certainly not satisfy the present demands of organic chemistry.

TUFTS COLLEGE, MASS.

ON SULPHON-FLUORESCEIN.

BY IRA REMSEN AND C. W. HAYES.

In a brief paper[1] published some time ago, one of us (R.) gave an account of experiments which were undertaken for the purpose of studying the action of phenols upon those aromatic acids which contain carboxyl and the sulphonic acid group in the ortho position relatively to each other. It was shown that by heating resorcin and ortho-sulpho-benzoic acid together, a product is obtained which is highly fluorescent, but it was not isolated. Since the time of the publication of the paper referred to, a number of efforts have been made in this laboratory to carry the investigation to a successful issue, but one difficulty after another has been encountered. Recently we have succeeded in preparing in pure condition the first representative of the class of substances which may be called *sulphon-phthaleins.* These compounds differ from the ordinary phthaleins simply in containing the group SO_2 instead of CO. While the latter are derived from the mother substance

$$C \begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4.CO \\ O \underline{\quad} \end{cases}$$, the sulphon-phthaleins are, in all probability,

derived from a substance of the formula $C \begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4.SO_2. \\ O \underline{\quad} \end{cases}$

[1] This Journal **6**, 180.

Preparation of Sulphon-fluorescein.—As the result of a number of experiments, the following method of preparing and purifying sulphon-fluorescein was found to give the best results.

Free, dry ortho-sulpho-benzoic acid is mixed with resorcin in the proportion of 1 part acid to 1.2 parts resorcin, or a slight excess of resorcin above that required assuming that the substances act upon each other in the proportion of 1 mol. weight of the acid to 2 mol. weights of resorcin. The mixture is put in a deep vessel, a large test tube or a small beaker, which is placed in a bath of sulphuric acid, a thermometer being supported in the mixture. The bath is gradually heated. At 100° the resorcin melts and the acid slowly dissolves in the liquid. No action appears to take place until the temperature reaches 175°, when water begins to be given off and the liquid slowly becomes darker in color. White crystals of resorcin collect on the sides of the vessel. After the heating has been continued for about seven hours at 178°–185°, the liquid has a clear deep red color, but shows no signs of becoming viscous. At length lustrous, yellow, crystalline plates appear in the liquid, and soon the whole mass becomes a thick, nearly solid yellow paste. Continued heating at the same temperature apparently causes no further change. The mass, which on cooling is made up of yellow crystals imbedded in a red viscous matrix, is then dissolved in hot water, in which it forms a clear red solution, or sometimes the solution contains a very small quantity of a brown flocculent precipitate. The solution is filtered, if necessary, and evaporated to a small volume, from which on cooling the substance separates in reddish yellow radial crystals. These are filtered and washed with ether till the washings are perfectly colorless. After repeated crystallisations from water the substance has a pale straw-yellow color, and when deposited slowly, forms transparent crystal blades, sometimes attaining a length of 2.6 mm. They are arranged in radial groups.

A considerable quantity of resorcin is lost by sublimation during the reaction, especially if the operation is carried on in a beaker, so that some excess should be added. But even when the resorcin is present in excess, at the end of the reaction some free acid is always left, and this can be obtained from the mother liquors in the characteristic colorless orthorhombic crystals.

The sulphur and the water of crystallisation, or at least the water

lost by the air-dried substance when heated to 123°, were determined. In estimating the water of crystallisation, the substance was heated to 106°–123° for about ten hours till it attained a constant weight. On standing in the air it quickly regained its original weight. When heated to 130°–140° for some time it turns slightly reddish and loses over 10 per cent. of its weight, which is not regained by standing in the air.

Estimation I of sulphur was made by Liebig's method, fusing with potassium hydroxide and potassium nitrate. Estimations II and III were made by Mr. C. Mindeleff, by a method devised by Professor Morse, which will be described by him later.

0.3882 gram heated to 106°–123° lost 0.0330 gram water $= 8.5$ per cent.

I. 0.2007 gram substance gave 0.1286 gram $BaSO_4$.

Estimations II and III gave 7.91 and 7.89 per cent. S respectively. The details were not furnished us, and are not at present available.

	Calculated for $C_{19}H_{12}O_6S + 2H_2O.$	Found.			
		I.	II.	III.	IV.
C	56.44	...	...	...	...
H	2.97	...	...	...	...
O	23.76	...	...	...	...
S	7.92	...	8.80	7.91	7.89
H₂O	8.91	8.5	...	...	...
	100.00				

These results show that in all probability the action of resorcin upon ortho-sulpho-benzoic acid is of the same kind as that of resorcin upon phthalic acid. Assuming that the anhydride of the acid is first formed, the reaction may be represented by the following equation:

$$C_6H_4{<}{CO \atop SO_2}{>}O + 2C_6H_4\left\{{OH \atop OH}{=}C\left\{{C_6H_3{<}{OH \atop O} \atop C_6H_3{<}{OH} \atop C_6H_4.SO_2 \atop O\text{---}\text{⌐}}\right. + 2H_2O.\right.$$
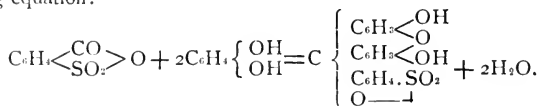
Properties of Sulphon-fluorescein.—Sulphon-fluorescein in many respects strongly resembles v. Baeyer's fluorescein, but it also differs from it very markedly in some of its properties. In water solution it shows a weak green fluorescence, which becomes much

stronger when the solution is rendered alkaline, but it is not by any means as strong as that of fluorescein. The dilute alkaline solution appears almost perfectly colorless by transmitted light, and by reflected light a clear green. Unlike fluorescein, it is extremely soluble in water, about one part in two or three of hot, and five or six of cold water. It is also soluble in absolute alcohol, forming a yellow solution with weak fluorescence. It is soluble with difficulty in ether, but when once in solution it is deposited only on evaporating to a small volume. It does not melt at 250°, but if kept at a lower temperature for a long time it becomes red, undergoing some decomposition. If quickly heated somewhat above 300° it melts to a deep red liquid and then solidifies. If the mass is treated with water it partly dissolves, leaving a dark brown flocculent precipitate which dissolves on the addition of an alkali, the solution having an intense fluorescence, nearly, if not quite, equal to that of fluorescein. This change produced by heating has not as yet been investigated.

The crystals are very thin blades, apparently monoclinic, showing the clino-pinacoid ∞ P ∞, and a very narrow prism ∞ P and clino-dome P $\check{\infty}$. The angle $\beta = 75°$, and the extinction angle against the c axis $= 20°$. The axial ratio could not be accurately determined.

Salts of Sulphon-fluorescein.—The influence of the group SO_2 on the chemical conduct of the compound is plainly shown by the fact that in water solution it decomposes carbonates and forms salts, which is not the case with fluorescein.

Barium salt.—Sulphon-fluorescein was boiled with an excess of carefully purified barium carbonate for two hours. The filtrate from the barium carbonate, evaporated to a small volume, deposited yellow crystals resembling the original substance, but in shorter and thicker prisms. These were twice recrystallised, and had then a light straw-yellow color. Every effort was made to secure the salt in perfectly pure condition before it was analysed, but notwithstanding this, the results obtained do not agree well with those required by the most probable formula.

I. 0.1843 gram salt gave 0.0498 gram $BaSO_4 = 15.90$ per cent. Ba.

II. 0.2620 gram salt gave 0.0708 gram $BaSO_4 = 15.89$ per cent. Ba.

Calculated for $(C_{19}H_{13}O_7S)_2Ba = 15.10$ per cent. Ba.

27

The water was estimated by heating at 110° until constant weight was reached. Only a part of the weight lost was regained by exposure to the air.

0.3943 gram salt lost 0.0286 gram at 110° $= 7.25$ per cent. water.

Calculated for $(C_{19}H_{12}O_7S)_2Ba + 4H_2O = 7.35$ per cent. water.

Although the analyses show a percentage of barium somewhat above that required by a compound of the formula $(C_{19}H_{12}O_7S)_2Ba$, still this appears to be the most probable formula for the compound. Assuming it to be correct, the first action in the formation of the salt must be the conversion of the anhydride sulphon-

fluorescein into the acid $C \begin{cases} C_6H_2 < ^{OH}_{O} \\ C_6H_2 < ^{O}_{OH} \\ C_6H_4.SO_2OH, \\ OH \end{cases}$ and the salt is derived

from this acid. The results obtained agree better with the percentage of barium required by the formula $(C_{19}H_{11}O_6S)_2Ba$ which is 15.38, but the only substance from which a salt of this composition

could well be formed has the constitution $C \begin{cases} C_6H_3 > O_2 \\ C_6H_3 \\ C_6H_4.SO_2OH. \\ OH \end{cases}$

Whether this is formed or not can only be determined by further experiments. By treating the salt with sulphuric acid the fluorescein is reformed.

Calcium salt.—Attempts were made to prepare the calcium salt, but without success. The sulphon-fluorescein was boiled several hours with very finely powdered Iceland spar, and some salt was formed, as shown by the evolution of carbon dioxide, but, on evaporating the solution and recrystallising the substance deposited, it was found to be the unchanged sulphon-fluorescein. There was some calcium salt in the mother liquors, but its extreme solubility prevented its separation.

Acetyl derivative of Sulphon-fluorescein.—Sulphon-fluorescein was boiled with an excess of acetic anhydride for about three hours. The solution became quite dark, and when evaporated on the water-bath it left a black tarry residue. This was treated with water, which dissolved a part, leaving a dark flocculent precipitate. The solution was boiled with bone-black and evaporated nearly to dryness. On cooling there separated a light yellow flocculent precipitate, which was very soluble in hot water and but

slightly less so in cold. This was dissolved in a small quantity of alcohol, from which it separated, on evaporation, in small radial crystals having a light lavender color and satiny lustre. They also have a peculiar odor resembling that of slippery elm, which is not removed by recrystallisation. They show a tendency to decompose, becoming yellow on exposure to the air. The substance does not melt or change in appearance under 245°. With alkalies it gives a slight greenish fluorescence. Not enough of it was obtained for the purposes of analysis. In all probability it is one of the possible acetyl derivatives of sulphon-fluorescein.

Bromine substitution-products of Sulphon-fluorescein.—When ordinary fluorescein is treated with bromine, a tetra-substitution-product is obtained most easily, and special precautions are necessary to obtain a product containing a smaller number of bromine atoms than four. With sulphon-fluorescein the case is different. It was dissolved in glacial acetic acid, in which it is soluble with some difficulty, and to the solution was added a 20 per cent. solution of bromine in acetic acid, in sufficient quantity to furnish eight atoms of bromine to one molecule of sulphon-fluorescein. This solution was evaporated on the water-bath, and, while still dilute, small, red, sharply defined crystals began to separate. The solution was evaporated to a small volume and allowed to cool, but nothing further separated. These crystals are difficultly soluble in water, alcohol, and ether. The alkaline solution shows a green fluorescence and slight red color by transmitted light. These crystals were dissolved in a large quantity of alcohol, and this solution, on evaporation, gradually deposited very small yellow crystals. These were dried in the air and analysed. The bromine was estimated by Carius' method.

I. 0.2345 gram substance gave 0.1718 gram $AgBr = 31.17$ per cent. Br.

II. 0.2786 gram substance gave 0.1815 gram $AgBr = 27.72$ per cent. Br.

Calculated for $C_{19}H_{10}Br_2O_6S = 30.42$ per cent. Br.

These results, though unsatisfactory, indicate that, under the given conditions, it is the di-brom-sulphon-fluorescein which is formed, and not the tetra-product, as in the case of ordinary fluorescein. Whether this is due to the presence of the group SO_2 or to the difficult solubility of the di-substitution-product cannot be decided at present.

When the original acetic acid mother liquor was evaporated to dryness, a red amorphous substance remained behind which had some resemblance to eosin. The concentrated alkaline solution had a deep red color without fluorescence, and acted as a red dye. The dilute alkaline solution showed the characteristic delicate pink of eosin.

Action of concentrated sulphuric acid on Sulphon-fluorescein.—A test tube in which sulphon-fluorescein was being made broke just at the end of the reaction, and allowed the contents to run out into the sulphuric acid bath, which had a temperature of $175°$. On standing several days a voluminous precipitate was deposited from the solution. This was separated by filtering through glass wool. When dry it formed a light yellow powder, extremely soluble in water, alcohol, and ether. The alkaline solution had an intense green fluorescence, with delicate shades of pink by transmitted light. On account of the extreme solubility it was found to be impossible to purify it by crystallisation. Hence the barium salt was made. The solution of the substance decomposed barium carbonate with great ease, and formed an easily soluble salt. When it was attempted to evaporate the solution of the salt to crystallisation, it was deposited in the form of a hard, insoluble, granular powder, which, on continued boiling of the solution, became brown. To avoid this the free acid was made from the barium salt by exactly precipitating the barium with sulphuric acid, and the calcium salt was then made by boiling the solution of the acid with finely powdered calcium carbonate. This also formed a hard, granular, insoluble powder on boiling, but did not change in color. As there was no guarantee of its purity and only a small quantity was obtained, it was not analysed.

Among other transformations of sulphon-fluorescein besides those already referred to, which were superficially studied, are those effected by concentrated hydrochloric acid and by reducing agents.

Concentrated hydrochloric acid does not dissolve sulphon-fluorescein, but converts it into a light yellow granular powder. When crystallised from water, in which it is quite easily soluble, it melts partially at $130°$, apparently with some decomposition. The compound was not further studied.

When treated with zinc dust in a strong alkaline solution, sulphon-fluorescein is reduced to a colorless substance, probably

analogous to fluorescin. On account of its great solubility it could not be obtained in the free state. It is quickly oxidised to sulphon-fluorescein by oxidising agents, as potassium permanganate and nitric acid, and passes back without further treatment if its solution be allowed to stand exposed to the air.

The investigation will be continued, and it is hoped that with a larger supply of material, some of the reactions above referred to may be cleared up.

Communication from the Chemical Institute of the University of Bonn.

CONTRIBUTIONS TO OUR KNOWLEDGE OF GLASER'S TWO MONOBROMCINNAMIC ACIDS.

By RICHARD ANSCHÜTZ AND CHARLES C. SELDEN.

Among the isomeric monobasic acids which bear to one another relations similar to those between fumaric and maleic acids, those which offer the greatest inducement for a more thorough investigation are the two monobromcinnamic acids discovered by Glaser.[1] We have, accordingly, been engaged for a considerable time on a comparative investigation of the derivatives of these acids, supplementing the work which one of us has done on fumaric and maleic acids. In this paper an account is given of some of the results obtained by us.

The Ethers of α- and β-Bromcinnamic Acids.

Barisch[2] showed some years ago that by treating β-bromcinnamic acid with alcohol and hydrochloric acid, the ethyl ether of α-brom-cinnamic acid is formed, analogous to the formation of ethers of fumaric acid from maleic acid, alcohol and hydrochloric acid. Since β-bromcinnamic acid as well as maleic acid may be changed by treatment with hydrochloric acid alone, into the other modification (the former into α-monobromcinnamic acid, the latter into fumaric acid), β-bromcinnamic acid may be compared with maleic acid as regards its action with alcohol and hydrochloric acid. If, on the other hand, instead of employing the free haloid acids for the formation of the ethers, we treat the silver salt of maleic acid

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[1] Annalen der Chemie **145**, 330.   [2] Journal prak. Chemie **20**, 182.

with alkyl iodides, there are in fact formed, as one of us has shown,[1] the alkyl ethers of maleic acid. We therefore treated the silver salt of β-bromcinnamic acid with alkyl iodides, a reaction which was first suggested by Barisch, and lately in the case of ethyl iodide carried out by Michael and Browne.[2]

The *methyl ether of β-bromcinnamic acid* may be made by the action of methyl iodide on the dry silver salt of β-bromcinnamic acid. It is a clear, rather oily liquid of a light yellow color. This ether, when saponified with very concentrated potash solution at a gentle heat, gave nearly pure β-bromcinnamic acid melting at $118°-119°$. It distilled under diminished pressure of about 10 mm. at $145°-147°$ (temperature of the paraffin bath $165°-170°$). By treatment with concentrated potash solution, this ether acted just as before the distillation, giving pure β-bromcinnamic acid. But if this methyl ether of β-bromcinnamic acid is heated under atmospheric pressure in a graphite bath, there distills at $286.5°-288.5°$ a liquid which is almost pure methyl ether of α-bromcinnamic acid, as was proved by its giving on careful saponification almost pure α-bromcinnamic acid.

Methyl ether of α-bromcinnamic acid, $C_6H_5C_2HBrO_2.CH_3$.— This ether, obtained as stated above, boils under a pressure of about 14 mm. at $158.5°-159.5°$ (temperature of paraffin bath $178°-183°$). On analysis the following figures were obtained:

I. 0.1954 gram substance gave on combustion with lead chromate 0.3632 gram CO_2 and 0.0673 gram H_2O.

II. 0.2465 gram substance gave 0.4561 gram CO_2 and 0.0868 gram H_2O.

	Calculated for $C_{10}H_9BrO_2$.	Found. I.	II.
C	49.79	50.69	50.46
H	3.73	3.83	3.91

In both analyses the carbon was found too high, an observation of which we shall hereafter speak more definitely.

The *ethyl ether of β-bromcinnamic acid*, $C_6H_5.C_2HBrO_2C_2H_5$, is prepared from the silver salt of β-bromcinnamic acid and ethyl iodide, and is also a clear, rather thick liquid of a light yellow color. Under about 10.5 mm. pressure it boils at $151.5°-153°$ (temperature of the paraffin bath $175°-182°$), and gives, on saponification with concentrated potash solution, pure β-bromcinnamic acid. Michael and Browne found the boiling point under 30 mm.

[1] Berichte der deutsch. chem. Gesell. **12**, 2282.   [2] Ibid. **20**, 550.

pressure to be 173°–174°; we found, under about 30 mm. pressure, the boiling point 176.5°–177° (temperature of the paraffin bath 195°–202°).

I. 0.1953 gram substance gave 0.1425 gram AgBr.

II. 0.1859 gram substance gave 0.1367 gram AgBr.

III. 0.2551 gram substance gave 0.4833 gram CO_2 and 0.1042 gram H_2O.

	Calculated for $C_{11}H_{11}BrO_2$.	I.	Found. II.	III.
C	51.76	...	...	51.67
H	4.31	...	...	4.53
Br	31.38	31.05	31.29	...

The *ethyl ether of a-bromcinnamic acid*, $C_6H_5C_8HBrO_2C_2H_5$, is formed by distilling the ethyl ether of β-bromcinnamic acid under ordinary pressure, at 293.5°–295.5° in a graphite bath. This, as will be seen, is about the same temperature as is given by Barisch and by Michael and Browne for the boiling point of the ethyl ether of a-bromcinnamic acid (made by them from a-bromcinnamic acid, alcohol and hydrochloric acid). As was observed during the rectification under diminished pressure, the ethyl ether of β-bromcinnamic acid had, in the distillation under ordinary pressure, undergone, in part, a further decomposition. The ethyl ether of a-bromcinnamic acid boiling at 159°–160.5° (temperature of the paraffin bath 185°), which was obtained by fractional distillation under a pressure of 10 mm., gave on analysis the following figures:

I. 0.2632 gram substance gave 0.5080 gram CO_2 and 0.1056 gram H_2O.

II. 0.2336 gram substance gave 0.4510 gram CO_2 and 0.0927 gram H_2O.

	Calculated for $C_{11}H_{11}BrO_2$.	I.	Found. II.
C	51.76	52.63	52.65
H	4.31	4.45	4.40

For the ethyl ether of a-bromcinnamic acid obtained from a-bromcinnamic acid, alcohol and hydrochloric acid, Michael and Browne give, under 30 mm. pressure, the boiling point 202°; under about 29.5 mm. pressure we found, however, 186.5°–188.5° to be the boiling point of the ethyl ether of a-bromcinnamic acid obtained by distillation of the ethyl ether of β-bromcinnamic acid. This ether (analysis above) gave, on careful saponification with

potash solution in the cold, α-bromcinnamic acid melting at $130°$–$131°$, which on analysis gave the following figures:

I. 0.1912 gram substance gave 0.3373 gram CO_2 and 0.0572 gram H_2O.

II. 0.1718 gram substance gave 0.3010 gram CO_2 and 0.0501 gram H_2O.

	Calculated for $C_9H_7BrO_2$.	I.	Found. II.
C	47.57	48.10	47.77
H	3.08	3.33	3.24

We are in doubt whether the transformation of the alkyl ethers of β-bromcinnamic acid into the alkyl ethers of the α-bromcinnamic acid is caused by the high temperature of distillation under common pressure. Both the ethers of α-bromcinnamic acid which were obtained by distillation showed on analysis a somewhat too high percentage of carbon. The explanation of this fact may be that hydrobromic acid had split off from a small portion of the ethers of bromcinnamic acid, thus forming the corresponding ethers of phenyl propiolic acid. The haloid acid thus set free could, perhaps, play an important part in the transformation of the ethers of β-bromcinnamic acid into the corresponding ethers of α-bromcinnamic acid.

In the following table are given the boiling points, under diminished pressure, of the four ethers of bromcinnamic acid which have been investigated:

			Pressure about.	Temperature of the bath.	Boiling point.
Methyl ether of β-bromcinnamic acid			11 mm.	165–$170°$	145 –$147°$
"	a-	"	14	178–183	158.5–159.5
Ethyl ether of β-		"	10.5	175–182	151.5–153
"	a-	"	10	185	159 –160.5

On comparing the α-bromcinnamic acid and β-bromcinnamic acid with fumaric acid and maleic acid, it is found that the α-acid evidently corresponds to fumaric acid and the β-acid to maleic acid. One of us has already shown[1] that the ethers of maleic acid boil at a higher temperature than the corresponding ethers of fumaric acid ; we should therefore expect to find the boiling points of the ethers of the β-acid higher than those of the ethers of the α-acid. But in reality it is just the reverse.

The *chloride of α-bromcinnamic acid*, $C_6H_5C_2HBrOCl$.—Before describing this compound, which is formed by the action of phos-

phorus pentachloride on both *α*- and *β*-bromcinnamic acid, we call attention to the results of a study of the action of phosphorus pentachloride on maleic acid which one of us made a short time ago in connection with Mr. Wirtz.[1] A compound was at that time obtained which boiled, under the same pressure, at a higher temperature than fumaryl chloride, and which gave, by analysis, figures agreeing with the formula $C_4H_2Cl_2O_2$. But this compound, although preserved in a sealed tube, underwent a change spontaneously, being apparently transformed into fumaryl chloride. The investigation of this reaction will soon be taken up again ; it was temporarily interrupted because it was found necessary first to become acquainted with the anilides of fumaric and maleic acids.

Our efforts to obtain from *β*-bromcinnamic acid a chloride different from that of *α*-bromcinnamic acid have been without success. Even when using salts of *β*-bromcinnamic acid instead of the free acid, a compound was obtained which in all its properties was identical with the chloride of *α*-bromcinnamic acid.

The chloride of *α*-bromcinnamic acid is a clear, oily, light yellow liquid which boils, under about 12 mm. pressure, at $152°-153°$ (temperature of the paraffin bath $177°$).

I. 0.1822 gram substance gave 0.2425 gram $AgCl + AgBr$ and 0.0016 gram Ag.

II. 0.1670 gram substance gave 0.2213 gram $AgCl + AgBr$ and 0.0014 gram Ag.

III. 0.2002 gram substance gave 0.3227 gram CO_2 and 0.0472 gram H_2O.

IV. 0.3197 gram substance gave 0.5173 gram CO_2 and 0.0727 gram H_2O.

	Calculated for C_9H_6BrClO.	I.	II.	Found. III.	IV.
C	43.99	…	…	43.97	44.13
H	2.44	…	…	2.62	2.52
Br + Cl	47.04	46.87	46.59	…	…

In contact with water, the chloride of *α*-bromcinnamic acid is very slowly transformed into *α*-bromcinnamic acid ; with ammonia it gives the amide, and with aniline the anilide of *α*-bromcinnamic acid, both of which are described below. The latter compound has been of special use in identifying the chloride obtained from *β*-bromcinnamic acid as the chloride of *α*-bromcinnamic acid.

The *amide of α-bromcinnamic acid*, $C_6H_5.C_3HBrO.NH_2$, is

[1] Berichte der deutsch. chem. Gesell. **18**, 1947.

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obtained by bringing together the chloride of α-bromcinnamic acid and an excess of aqueous ammonia. It crystallises from hot water, in which it is difficultly soluble, in the form of very thin leaves possessing a pearly lustre. Melting point 118.5°–119°.

I. 0.1651 gram substance gave 0.1371 gram AgBr.

II. 0.0839 gram substance gave 0.0690 gram AgBr.

III. 0.2649 gram substance gave 14 ccm. N at 16.5° and under 756.45 mm. pressure.

	Calculated for C_9H_8BrNO.	I.	Found. II.	III.
Br	35.40	35.33	35.00	...
N	6.19	...	...	6.10

Anilide of α-bromcinnamic acid, $C_6H_2C_3HBrONH.C_6H_5$.—This compound is formed by the action of aniline on the chloride of α-bromcinnamic acid, a reaction by which considerable heat is evolved. It crystallises from alcohol in the form of little white needles melting at 80°. On standing for a number of days in the alcoholic mother liquor, these needles change of their own accord into six-sided plates, the melting point, however, remaining unaltered.

I. 0.1845 gram substance gave 0.1135 gram AgBr.

II. 0.2264 gram substance gave 0.1402 gram AgBr.

	Calculated for $C_{15}H_{12}BrNO$.	I.	Found. II.
Br	26.49	26.18	26.35

NOTE.— In the paper on "The Isomerism of Fumaric and Maleic Acids" (this Journal 9, 253) I have attempted to prove for these substances the following formulas:
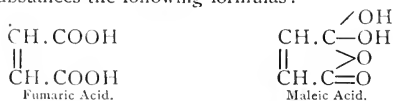
The idea suggests itself that the isomerism between the two monobromcinnamic acids may be explained by analogous constitutional formulas, thus:
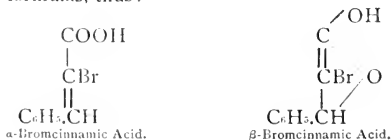
For the present, however, I place no special value upon these formulas, because their only support is that they make it possible to present the distant analogy with the above expressions for fumaric and maleic acids. As in the case of the last two named acids, so also in that of the α- and β-bromcinnamic acids, there is only one way to decide, that being by experimental investigation. I hope soon to be in a position to communicate the results of some researches made in the above mentioned direction.—ANSCHÜTZ.

NOTES.

Quadrivalence of Tellurium towards Chlorine.

A. Michaelis has determined the specific gravity of the vapor of tellurium tetrachloride, and has found that it corresponds to the formula $TeCl_4$, even when the vapor is heated far above the boiling point of the compound. The determinations were made at the temperature of boiling sulphur and that of boiling phosphorus pentasulphide. It is interesting to note how the stability of the tetrachlorides of the members of the sulphur group increases with the atomic weight. Sulphur tetrachloride exists only in liquid condition below $21°$; selenium tetrachloride breaks down into the monochloride and chlorine when heated to boiling: $2SeCl_4 =$ $Se_2Cl_2 + 3Cl_2$.—(*Berichte der deutschen chemischen Gesellschaft* **20,** 1780.)

On Potassium Germano-fluoride.

The fact that germanium is a member of the silicium group suggests the possibility of preparing a salt of the formula K_2GeF_6, analogous to potassium fluo-silicate, K_2SiF_6. Gerhardt Krüss and L. F. Nilson have made the salt by dissolving germanium oxide in hydrofluoric acid and adding potassium fluoride to the solution. The salt resembles the corresponding silicium salt very closely, having the composition represented by the above formula. As regards solubility it lies between the silicium salt and the corresponding tin salt; just as the position of germanium itself in the periodic system is between that of silicium and that of tin. In his paper on the periodic law which appeared in 1870,[1] Mendelejeff, in describing the properties of the then unknown eka-silicium, said : " There is no doubt that eka-silicium will yield a series of

[1] Annalen der Chemie, Sup. **8,** 201.

double fluorides (K_2EsF_6) isomorphous with the corresponding salts of silicium, titanium, zirconium, and tin.   The potassium salt will be more soluble in water than the corresponding silicium salt. Eka-silicium fluoride, like titanium, zirconium, and tin fluorides, TiF_4, ZrF_4, and SnF_4, will not be a gas."—(*Berichte der deutschen chemischen Gesellschaft* **20,** 1698.)

On the Removal of Arsine from Hydrogen Sulphide.

For the purification of hydrogen sulphide made from the ordinary reagents, O. Jacobsen recommends passing the gas over some solid iodine before it is washed with water.   This method is based upon the well-known facts that arsine and iodine react violently at the ordinary temperature, forming arsenic triiodide and hydriodic acid, while hydrogen sulphide does not act at all upon iodine in the solid state or disolved in strong hydriodic acid.   Experiment showed that 2 to 3 grams of iodine were sufficient completely to purify a current of hydrogen sulphide made from the ordinary reagents, and running uninterruptedly for a day.   The iodine is coarsely powdered, dried in the air, and then placed in a comparatively narrow glass tube, 30-40 cm. in length, a layer of glass wool being put at each end.   In chemico-legal examinations, it is recommended that a second shorter tube containing some iodine be introduced, and that after the analysis this be sealed and put aside.   If it can be shown that the iodine in this second tube contains no arsenic, evidence will thus be furnished that the hydrogen sulphide used was pure.   It is not advisable to dry the iodine thoroughly, as the reaction is aided by the formation of a thin layer of a solution of iodine on the particles of iodine.   If it is desired to purify hydrogen, this should first be passed over iodine as above described, then over glass wool which is moistened with a concentrated solution of potassium iodide, and finally washed with caustic potash.—(*Berichte der deutschen chemischen Gesellschaft* **20,** 1999.)

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ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

II.—ON THE CONDUCT OF THE SALTS OF DIAZO-BENZENE AND OF THE THREE DIAZO-TOLUENES TOWARD ALCOHOL.

By Ira Remsen and W. R. Orndorff.

The fact that under some circumstances diazo compounds when boiled with alcohol do not decompose in such a way as to form compounds in which hydrogen takes the place of the diazo group, has of late been frequently commented upon, but no generalisation has been reached touching the conditions which give rise to the abnormal reaction. We accordingly decided to begin a thorough investigation of the subject, with the object more particularly of discovering, if possible, the conditions which are favorable to the two kinds of decomposition of diazo compounds with alcohol. The plan which we have thus far followed, and which it is proposed to follow further, is to study with care the decomposition of a number of the simplest diazo compounds of the aromatic group. We naturally began with diazo-benzene, using both the nitrate and sulphate. We then studied the diazo compounds formed from the three isomeric toluidines. The three isomeric aniline-sulphonic acids, the nitranilines, the amido-benzoic acids, chlor-anilines, etc., will also be studied in due time, and thus, it is hoped, the material will be furnished for generalisations. In this paper the decomposition of diazo-benzene nitrate and sulphate, and of the sulphates of ortho, meta, and para-diazo-toluene is the subject treated.

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Decomposition of diazo-benzene nitrate by alcohol.—Diazo-benzene nitrate was made without difficulty by the method described by Griess. The crystallised compound was quickly filtered off with the aid of the pump, washed with absolute alcohol until this ran through perfectly colorless, and then with anhydrous ether. When all the wash liquid had drained off, the salt was placed on drying paper and the ether allowed to evaporate at the temperature of the room. When the odor of the ether was no longer perceptible, the salt was placed in a vacuum desiccator over sulphuric acid. Thus prepared, it is a beautiful white salt, crystallised in long needles. In dry condition it can be kept for five to six hours without undergoing change, but if kept longer it rapidly turns brown and acquires an odor resembling that of ortho-nitro-phenol.

For the decomposition with alcohol, 20 grams of pure dry diazo-benzene nitrate were taken at a time. It was placed in a dry balloon flask of one litre capacity, and 200 cc. of absolute alcohol added, the flask connected with an inverted condenser, and gently heated on a water-bath. Decomposition began at a comparatively low temperature, from 50° to 60°, and was allowed to proceed without further application of heat. Nitrogen was given off freely, but no odor of aldehyde could be detected during the entire experiment. The water in the bath was finally heated to boiling, to ensure complete decomposition. 265 grams of the dry nitrate were decomposed in this way. The different portions of liquid left in the flask were united and the alcohol distilled off from a water-bath. This alcoholic distillate did not have the odor of aldehyde such as is frequently noticed in the alcoholic distillate in the case of the decomposition of a diazo compound by alcohol. It was colored slightly yellow and had a pleasant aromatic odor. On diluting it with about six times its volume of a saturated solution of sodium chloride, a light yellow oil rose to the top. This was separated, washed with caustic soda solution, then with water, dried over calcium chloride, and subjected to fractional distillation. Two colorless oils were obtained, one boiling at 80°–81°, the other at 168°–170°. The former was shown to be benzene; the latter was phenetol.
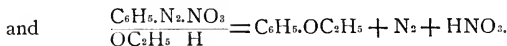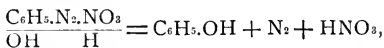
The tarry mass left in the flask after distilling off the alcohol was treated with an excess of caustic soda solution and distilled in a current of steam. A yellow oil, lighter than water and with a pleasant

aromatic odor, passed over. This boiled constantly at 170° and had the other properties of phenetol.

The contents of the flask, through which steam had been passed, were then acidified with sulphuric acid and again subjected to distillation in steam. A yellow crystalline solid passed over with the steam. On purification this was found to have the melting point 45° and the other properties of ortho-nitro-phenol. The solution remaining in the flask was then filtered, boiled with bone black, evaporated to half its volume, and allowed to crystallise. The crystals after purification melted at 114° and had the general properties of dinitro-phenol.

Besides the products mentioned, a considerable quantity of tarry matter was obtained, and from this nothing with definite properties could be isolated.

As regards the quantities of the products formed in the decomposition, the result was unexpected. From the 265 grams of nitrate decomposed there were obtained 42 grams of phenetol, 5 grams of benzene, 20 grams of ortho-nitro-phenol, and 10 grams of dinitro-phenol. It will be seen that the principal reaction which takes place when diazo-benzene nitrate is decomposed with alcohol is that which gives phenetol, while that which gives benzene takes place to a very much smaller extent. In other words, in the case of the simplest aromatic diazo compound the decomposition with alcohol is for the most part strictly analogous to the decomposition with water, the two reactions being represented by the equations,

$$\frac{C_6H_5.N_2.NO_3}{OH \quad H} = C_6H_5.OH + N_2 + HNO_3,$$

and

$$\frac{C_6H_5.N_2.NO_3}{OC_2H_5 \quad H} = C_6H_5.OC_2H_5 + N_2 + HNO_3.$$

It is evidently necessary that some of the five hydrogen atoms of the benzene should be replaced in order that the reaction shall take place in the other way.

The formation of ortho-nitro-phenol and dinitro-phenol was noticed by Griess, and he attributed their presence to the action of water, as he used ordinary alcohol. But in our experiments special care was taken to avoid the presence of water, and it is difficult to see, therefore, how phenol could first have been formed, and then converted into nitro derivatives by the action of the nitric acid liberated in the reaction.

It seemed possible that the ortho-nitro-phenol might be formed by elimination of the nitrogen and a rearrangement of the constituents of the molecule without the intervention of water, as indicated in this equation,

$$C_6H_5.N_2.NO_3 = C_6H_4 \left\{ {OH \atop NO_2} + N_2 \right.$$
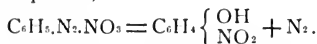
To test this hypothesis, a quantity of pure, dry diazo-benzene nitrate was decomposed by gently heating it in pure, dry toluene.

Decomposition of diazo-benzene nitrate by heating in toluene.—
15 grams of dry diazo-benzene nitrate were placed in a flask, and 250 cc. of anhydrous toluene which had been dried over sodium were added. The flask was then placed in a water-bath and the bath gradually heated. The flask must be constantly shaken and the temperature of the bath kept as low as possible. The nitrate soon began to give up nitrogen, became amorphous in form, and stuck to the sides of the flask, the toluene acquiring a deep red color. An excess of solution of sodium carbonate was then added, the toluene separated, and the sodium carbonate solution boiled for some time to get rid of toluene. The solution was placed in a large balloon flask, neutralised with sulphuric acid, and distilled with steam. A yellow crystalline solid came over. This was crystallised from alcohol and found to melt at 45°, and had the other properties of ortho-nitro-phenol. From the 15 grams of the nitrate 3 grams of ortho-nitro-phenol were obtained, and in another experiment in which 16½ grams of the nitrate were used, 4 grams of ortho-nitro-phenol were obtained. As, when the decomposition was effected in alcohol only 30 grams of ortho-nitro-phenol and dinitro-phenol together were obtained from 265 grams of the nitrate, it will be seen that a larger proportion of the nitrate undergoes this peculiar decomposition when toluene is used as the medium. These experiments make it highly probable that the formation of the substituted phenols in the decomposition of diazo-benzene nitrate with absolute alcohol is due not to the formation of phenol and the action of nitric acid upon this, but to the elimination of the nitrogen and the rearrangement of the constituents of the molecule in such a way that the linking oxygen enters the benzene molecule as hydroxyl and the nitro group takes the ortho position with reference to it:

$$C_6H_4 \left\{ {H \atop N_2 - O - NO_2} = C_6H_4 \left\{ {OH \atop NO_2} + N_2 \right. \right.$$
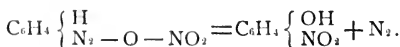
The toluene used in the experiment was carefully examined for the presence of para-nitro-phenol, but not a trace of this was found, nor was any dinitro-phenol found.

The action of dilute (50 per cent.) alcohol on diazo-benzene nitrate was next tried, and it was found that the yield of phenetol was smaller, while that of the nitro-phenols was larger than was obtained in the experiments in which absolute alcohol had been used. The quantity of benzene formed was so small that it could not be isolated.

Decomposition of diazo-benzene sulphate by alcohol.—After many methods had been tried, the following was adopted for the preparation of diazo-benzene sulphate : 25 grams of the finely powdered aniline nitrate are converted into diazo-benzene nitrate, and the solution of this nitrate quickly filtered. The solution is then placed in a vessel of ice water, and an excess of concentrated sulphuric acid added, drop by drop, from a glass-stoppered burette, the flask being shaken after the addition of each drop to prevent an elevation of temperature and decomposition of the diazo compound. After adding the sulphuric acid the solution is again filtered, and then poured into twice its volume of absolute alcohol surrounded by a freezing mixture. Ether is then added until the concentrated aqueous solution of the sulphate separates in a thin layer at the bottom. The aqueous solution is then separated and again treated with alcohol and ether, and then placed in a freezing mixture. The diazo-benzene sulphate soon crystallises out, sometimes in beautiful white needles, and at others in short prisms. The crystals are filtered off and washed with absolute alcohol, and afterwards with anhydrous ether. After pressing between layers of bibulous paper, they are put in the vacuum desiccator over sulphuric acid. Thus prepared, the diazo-benzene sulphate is a beautiful white crystalline salt, very soluble in water, and almost insoluble in anhydrous ether. It is more stable than the nitrate, but like it, turns brown when kept over a day exposed to the air.

136 grams of the sulphate were decomposed in portions of about 20 grams each in the same way as the nitrate. The alcohol in which the decomposition took place did not have the odor of aldehyde. From the 136 grams of sulphate there were obtained 40 grams of phenetol and 2 grams of benzene. The yield of phenetol is therefore better with the sulphate than with the nitrate.

Phenetol.—The boiling point of phenetol is given by Boly[1] at
175°, while Cahours[2] gives it at 172°. A careful determination of
the boiling point, using a carefully calibrated Zincke thermometer,
gave 170°. The specific gravity, determined by means of a
Mohr-Westphal balance, was found to be 0.973 at 15°. When
treated with fuming nitric acid, dinitro-phenetol is very readily
formed. This melts at 86°–87°, and somewhat resembles dinitro-
benzene, which melts at 89.9°. As Griess obtained a compound
melting at 89° on treating the oil from the alcoholic distillate with
fuming nitric acid, he concluded that this was dinitro-benzene, and
hence he states that benzene is the principal product of the decom-
position of the salts of diazo-benzene with alcohol.

Decomposition of diazo-benzene sulphate by heating in toluene.—
The formation of ortho-nitro-phenol by heating diazo-benzene
nitrate in toluene suggested that a similar decomposition of the
sulphate might take place, giving rise to the formation of one of
the phenol-sulphonic acids. 5½ grams of the sulphate were accord-
ingly treated as above described in the case of the nitrate, care
being taken to prevent the temperature from rising above 50°.
The sulphate decomposed slowly, with evolution of nitrogen, and
was finally converted into a brownish heavy oil which separated
from the toluene and settled at the bottom of the flask. A solution
of potassium carbonate was then added and the toluene separated.
The solution was then boiled to free it entirely from toluene,
filtered from tarry matter, and evaporated to dryness. The residue,
which consisted chiefly of potassium sulphate, was extracted
several times with alcohol, and from the alcoholic solution thus
obtained, short needle-shaped crystals having the general appear-
ance of potassium para-phenol-sulphonate were deposited on
evaporation. The aqueous solution of this substance gave a violet
color with ferric chloride. A potassium estimation gave the
following result :

0.272 gram salt gave 0.1094 gram K_2SO_4.

	Calculated for $C_6H_4{<}{OH \atop SO_3K}$.	Found.
K	18.43	18.05

Unfortunately for our purpose, potassium toluene-sulphonate,
$C_6H_4{<}{CH_3 \atop SO_3K}$, contains very nearly the same percentage of

[1] Journal of Chemical Society **2,** 28.   [2] Annalen der Chemie **74,** 314.

potassium as the phenol-sulphonate, and it appeared possible that the sulphuric acid set free from the sulphate might have acted upon the toluene to form the sulphonic acid. If the salt were the toluene-sulphonate, then by treating it with phosphorus pentachloride and ammonia it should easily be converted into the sulphonamide, which could be recognised by its melting point. On treating the salt in this way, however, no sulphonamide was obtained. Taking into consideration this fact, together with the color reaction with ferric chloride, the evidence that the salt is the phenol-sulphonate is fairly satisfactory.

In another experiment 12 grams of the sulphate were decomposed as before in toluene. After the decomposition was complete, water and barium carbonate were added. The toluene was then poured off and the liquid boiled for some time. After filtering it was treated with bone black and again filtered. Potassium carbonate was then added until the solution had a slightly alkaline reaction; the solution filtered and evaporated to dryness. The salt thus obtained was heated for several hours to 140°–150° with an excess of benzoyl chloride. After the excess of the benzoyl chloride had been evaporated off, the dry mass was treated with ether to dissolve benzoic acid. The potassium salt was then dissolved in water and a slight excess of barium chloride solution added. A barium salt was thus obtained which was easily soluble in hot water, but almost insoluble in cold water. From the solution in hot water it was deposited in beautifully crystallised form. After recrystallisation it was found to have the properties of barium benzoyl-para-phenol-sulphonate as given by Engelhardt and Latschinoff.[1] Its analysis gave the following results:

I. 0.3272 gram salt gave 0.1097 gram $BaSO_4$.

II. 0.4092 gram salt gave 0.1377 gram $BaSO_4$.

	Calculated for $(C_{13}H_9SO_5)_2Ba$.	Found. I.	II.
Ba	19.80	19.70	19.77

These results leave no doubt that when diazo-benzene sulphate is decomposed by heating in toluene it undergoes to some extent a decomposition analogous to that of the nitrate, the product being para-phenol-sulphonic acid. The change is represented in the following equation:

$$C_6H_4 \left\{ \begin{array}{l} H \\ N_2 \end{array} \right. - O - SO_3H = C_6H_4 \left\{ \begin{array}{l} OH \\ SO_3H \end{array} \right. + N_2.$$
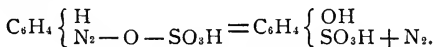
[1] Zeitschrift für Chemie **4,** 78.

The fact that the para acid is obtained while ortho-nitro-phenol is the product of the decomposition of the nitrate is not surprising, in view of the ease with which ortho-phenol-sulphonic acid is converted into the para acid by heat.

Decomposition of ortho-diazo-toluene sulphate by alcohol.—The preparation of ortho-diazo-benzene sulphate presents no serious difficulties. The method which was found to give the most satisfactory results was the following: 25 grams pure ortho-toluidine were dissolved in 250 cc. ordinary alcohol, and an excess (25 grams) of concentrated sulphuric acid gradually added. Heat is then applied until all the ortho-toluidine sulphate has passed into solution. The flask containing the alcoholic solution is then placed in ice water and a current of nitrogen trioxide passed through it. In a short time the *o*-diazo-toluene sulphate crystallises out. It is quickly filtered off, washed with absolute alcohol until this runs through colorless, and then with anhydrous ether. When all the ether has drained off, the sulphate is placed upon bibulous paper. The salt, which when first brought on the filter is perfectly white, turns bluish green on the surface when washed with alcohol, and after the evaporation of the ether it has a tendency to turn red.

The salt was decomposed in alcohol as in the case of diazo-benzene nitrate, 20 grams being used at a time. The odor of aldehyde could not be detected during the entire course of the experiment. 44 grams of the sulphate were thus decomposed. When the alcohol was distilled off on a water-bath, and diluted with about six times its volume of water, an oil rose to the top. This was separated, washed, and dried over fused calcium chloride, and found to boil at 180°. After all the alcohol was distilled off, water was added and the mixture distilled in steam. An oil which was lighter than water passed over, and this proved to be identical with that obtained from the alcohol. Its properties are those of *o*-cresol ethyl ether.[1] With nitric acid it yielded a nitro compound melting at 72°, identical with the mono-nitro derivative of the ethyl ether of ortho-cresol described by Staedel.[2] From the 44 grams of the sulphate decomposed, 13 grams of the ethyl ether were obtained, and no toluene could be detected. It is evident, therefore, that when ortho-diazo-toluene sulphate is decomposed by heating in alcohol, the principal reaction which takes place is that

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[1] Berichte der deutsch. chem. Gesell. **11**, 898.   [2] Annalen der Chemie **217**, 155.

which yields the ethoxy derivative, and in this respect the compound acts like the salts of diazo-benzene.

Decomposition of para-diazo-toluene sulphate by alcohol.— Para-diazo-toluene sulphate was prepared in the same way as the ortho compound. Thus prepared it is a beautiful white salt, crystallising in thin scales or plates, having no odor and being comparatively stable. It may be kept for weeks if dry and not exposed to the light. If it is moist, or if exposed to the light, it gradually turns brown.

The decomposition in alcohol began at 75°. The odor of aldehyde was at once noticed and continued throughout the course of the experiment. 70 grams of the para-sulphate were decomposed, the residues united, and the alcohol distilled off from a water-bath. This alcoholic distillate smelled strongly of aldehyde, and an oil separated from it when about six times its volume of water was added. On purifying the oil and distilling it, it separated into two fractions, one boiling at 110°, the other at 186°–187°. By distilling in steam the residue left after the alcohol was distilled off, a further quantity of oil was obtained, which proved to be identical with the higher boiling one obtained from the alcohol. The substance boiling at 110° is toluene, the other is the ethyl ether of para-cresol,[1] as was shown by the boiling point, and by the conversion of the substance into para-ethoxy-benzoic acid,[2] melting at 195°, by oxidising with potassium permanganate.

From 70 grams of para-diazo-toluene sulphate, 13 grams of toluene and 8 grams of the ethyl ether of para-cresol were obtained. In this case, then, the presence of the methyl group in the para position to the diazo group causes the decomposition in alcohol to take place in an entirely different way from that in which it takes place when the methyl group is not present.

Decomposition of meta-diazo-toluene sulphate by alcohol.— Meta-toluidine was prepared according to the directions of Cosack,[3] by starting with para-toluidine, making the acetyl derivative, treating this with fuming nitric acid and thus making the mono-nitro derivative, eliminating the amido group, and reducing the meta-nitro-toluene by means of stannous chloride and hydrochloric acid.

The transformation of the nitro-para-toluidine into meta-nitro-

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[1] Berichte der deutsch. chem. Gesell. **2**, 624 ; and Zeitschrift für Chemie, 1869, 619.
[2] Annalen der Chemie **141**, 254.   [3] Inaugural Dissertation.

toluene takes place easily and a good yield is obtained. The yield from 192 grams was 119 grams, or 68.7 per cent. This indicates that the presence of the nitro group in the meta position relatively to the methyl, and in the ortho position relatively to the diazo group, is favorable to the introduction of hydrogen in the place of the diazo group in the decomposition with alcohol.

The preparation of meta-diazo-toluene sulphate was carried on as follows : 18 grams of meta-toluidine were dissolved in 200 cc. of absolute alcohol, an excess (about 20 grams) of concentrated sulphuric acid added, and the flask heated until all the sulphate dissolved. The flask was then placed in ice water and a rapid current of nitrogen trioxide passed through. After some time the diazo sulphate crystallised out in small, beautiful white plates, which rapidly turned red on exposure to the air. It was filtered off, and washed first with absolute alcohol and then with anhydrous ether. On account of its instability it was decomposed at once with alcohol. This decomposition was carried on exactly as in the case of the ortho and para compounds. The odor of aldehyde was not noticed during the experiment, nor in the alcoholic distillate. From the alcoholic distillate and from the residue on heating in a current of steam, an oil was obtained which boiled at 190° and is the ethyl ether of meta-cresol.[1] This was shown to be the case by oxidising a small quantity of the oil with potassium permanganate, when it was converted into meta-ethoxy-benzoic acid[2] melting at 137°.

18 grams of meta-toluidine gave 10 grams of the ethyl ether and no toluene.

Summary.—Diazo-benzene nitrate when decomposed in alcohol yields mainly phenetol and only a very small quantity of benzene. At the same time, not inconsiderable quantities of ortho-nitro-phenol and dinitro-phenol are formed.

The substituted phenols are formed by the elimination of the nitrogen and a rearrangement of the constituents of the molecule ; as was shown by the experiments on the decomposition of diazo-benzene nitrate and sulphate in toluene, para-phenol-sulphonic acid being formed in the latter case.

Diazo-benzene sulphate decomposes in essentially the same way as the nitrate, though the yield of phenetol is somewhat larger.

[1] Berichte der deutsch. chem. Gesell. **8**, 887.

[2] Oppenheim and Pfaff, Berichte der deutsch. chem. Gesell. **8**, 888. Heintz, Annalen der Chemie **153**, 333.

When ortho-diazo-toluene sulphate is decomposed in alcohol, about 50 per cent. is converted into the ethyl ether of ortho-cresol.

When meta-diazo-toluene sulphate is decomposed, about 40 per cent. is converted into the ethyl ether of meta-cresol and no toluene is formed.
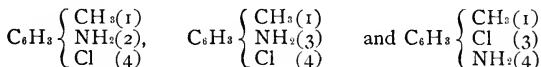
When para-diazo-toluene sulphate is decomposed, about 45 per cent. is converted into toluene and 18 per cent. into the ethyl ether of para-cresol.

The figures given are of course only approximately correct, but, as great care was taken in all the processes, they will serve to give a general idea of the course of the reactions in the cases studied.

Study of Recorded Cases.—There are on record a great many cases of the decomposition of diazo compounds by means of alcohol, and a thorough study of the literature was made in the hope of getting some clue to the law governing this kind of decomposition. Unfortunately, but few of these cases have been studied with the care which is desirable for our purpose, so that it is frequently impossible to decide whether only one product is formed or not, and in what quantity.

Our experiments appear to show that the presence of a paraffin residue in the para position relatively to the diazo group is favorable to the replacement of the diazo group by hydrogen, and that the presence of an acid group in the meta position to the paraffin residue and the ortho position to the diazo group is still more favorable to this reaction, which, for convenience, we may call the hydrogen reaction.

E. Wroblewsky[1] has called attention to the fact that, when the three isomeric chlortoluidines of the structures represented by these formulas,

$$C_6H_3 \begin{cases} CH_3(1) \\ NH_2(2), \\ Cl \quad (4) \end{cases} \qquad C_6H_3 \begin{cases} CH_3(1) \\ NH_2(3) \\ Cl \quad (4) \end{cases} \qquad \text{and } C_6H_3 \begin{cases} CH_3(1) \\ Cl \quad (3) \\ NH_2(4) \end{cases}$$

are converted into diazo compounds and these treated with alcohol, the first two yield ethoxy derivatives and the third yields meta-chlor-toluene. He concludes that " in the decomposition of the diazo compounds by alcohol, the normal reaction (i. e. the Griess or hydrogen reaction) suffers a change due to the influence of the halogen replacing the hydrogen, but only in those cases in

[1] *Zeitschrift für Chemie* **6**, 164; and *Berichte der deutsch. chem. Gesell.* **9**, 38, and **17**, 2703.

which the halogen occupies the para position relatively to some other substituting group." In the light of our experiments on the three toluidines, it is evident that Wroblewsky's conclusion is not justified. The character of the decomposition is largely determined by the position of the diazo group relatively to the methyl group.

Ladenburg[1] obtained a compound soluble in alcohol by treating an alcoholic solution of nitro-toluylene-diamine with nitrogen trioxide. On boiling the alcoholic solution of the diazo compound thus formed, nitrogen was evolved and an ethyl ether of nitro-cresol was formed. The structure of the nitro-toluylene-diamine as shown by Staedel[2] is represented by the formula $C_6H_2\begin{cases} CH_3\,(1) \\ NH_2(2) \\ NH_2(4) \\ NO_2(5) \end{cases}$, and the ethyl ether of nitro-cresol obtained by Ladenburg has, according to Staedel, the structure $C_6H_2\begin{cases} CH_3\quad(1) \\ OC_2H_5\,(2). \\ NO_2\quad(5) \end{cases}$

In this case the diazo group in the para position relatively to methyl is replaced by hydrogen, while the other, which is in the ortho position relatively to methyl, is replaced by the ethoxy group.

Schmitt[3] found that the diazo compound from para-sulphanilic acid, when boiled with alcohol under pressure, gave benzene-sulphonic acid. Ador and Meyer[4] confirm Schmitt's results and state that the yield of benzene-sulphonic acid is very satisfactory. Hybbenerth[5] has shown that the diazo compound of meta-sulphanilic acid also yields the corresponding benzene-sulphonic acid. In this case the sulpho group in the para and meta positions appear to exert the same influence whether in the para or meta position. The case of the meta acid requires further investigation.

A curious case which appears to show that the influence of methyl is stronger that that of carboxyl is that described by Remsen and Broun.[6] They showed that the diazo compound from the amido-toluic acid of the structure $C_6H_3\begin{cases} CH_3\quad(1) \\ NH_2\quad(2), \\ COOH\,(5) \end{cases}$ is converted quantitatively into the corresponding ethoxy compound, $C_6H_3\begin{cases} CH_3\quad(1) \\ OC_2H_5\,(2). \\ COOH\,(5) \end{cases}$ Here, although the carboxyl is in the para

[1] Berichte der deutsch. chem. Gesell. **7**, 1212.   [2] Annalen der Chemie **217**, 155.
[3] Annalen der Chemie **120**, 153.   [4] Ibid. **159**, 9.   [5] Ibid. **221**, 205.   [6] This Journal **4**, 374.

position relatively to the diazo group, only the ethoxy reaction takes place, in consequence, probably, of the presence of the ortho-methyl.

There are on record eleven cases of amido compounds which contain besides the amido group one other substituting group, the diazo compounds of which undergo the hydrogen reaction with alcohol. Of these eleven cases, eight contain the amido group in the para position, one in the meta and two in the ortho position. The two latter are naphthalene derivatives, in which the conditions are more complicated than in the benzene derivatives.

Besides the simple cases just referred to, between eighty and ninety other cases in which two and more groups besides the amido group are present are recorded. An examination of these shows that in nearly all cases in which the hydrogen reaction takes place, the amido group is in the para position to some other group; while in most cases in which the phenetol reaction takes place, the amido group is in the ortho or meta position relatively to some other group. Many of these complex cases are, however, not well adapted to the purposes of this investigation, at least not until the simpler cases have been thoroughly investigated and the character of the influence exerted by different atoms and groups in different positions is known.

ON THE PREPARATION OF ORTHO-SULPHO-BENZOIC ACID.

By R. N. Brackett and C. W. Hayes.

For the purposes of investigations which we desired to undertake at the suggestion of Professor Remsen, a supply of ortho-sulpho-benzoic acid and of benzoic sulphinide was necessary. As the methods at command for the preparation of these substances are not very satisfactory, we made a number of experiments with the object of finding, if possible, some more satisfactory method than any now known. The results obtained are described in the following paper.

Remsen and A. G. Palmer[1] endeavored to simplify the prepara-

[1] This Journal **8,** 243.

tion of ortho-toluene-sulphonic acid by making the sulphonic acid of para-nitro-toluene, which has the constitution represented by the formula $C_6H_3 \begin{cases} CH_3 \\ SO_3H \ (o) \\ NO_2 \ \ (p) \end{cases}$ and then eliminating the nitro group by means of the diazo reactions ; but they found that when the diazo-sulphonic acid, $C_6H_3 \begin{cases} CH_3 \\ SO_2 \\ N_2 \end{cases} >$, is boiled with alcohol, a considerable

proportion of it is converted into the ethoxy compound $C_6H_3 \begin{cases} CH_3 \\ SO_3H \\ OC_2H_5 \end{cases}$ and but a small quantity of the desired ortho-toluene-sulphonic acid is obtained. It was therefore determined first to try the reaction described by S. Haller, which consists in converting the diazo compound into the corresponding hydra-zine compound and treating this with a dilute solution of copper sulphate.

Para-nitro-toluene is easily converted into the sulphonic acid by treating it with three times its weight of fuming sulphuric acid on a water-bath. It was found convenient to make the potassium salt, as this crystallises well, and its solubility is such that it can easily be separated from its solutions.

Reduction of para-nitro-toluene-ortho-sulphonic acid.—The method of reduction first used consisted in adding ammonia to the water solution of the salt, and then saturating with sulphuretted hydrogen. On the large scale this method does not work satis-factorily, as the presence of the sulphur compounds of ammonia in the solution interfere with the complete separation of the amido acid in pure condition. It was found much better to use tin and hydrochloric acid. The reduction was conducted as follows : 5 parts by weight of the salt, 6 parts of granulated tin, and 30 parts of ordinary concentrated hydrochloric acid were placed together in a large evaporating dish. The dish was heated gently until the reaction began, then the lamp was turned out and the mixture stirred occasionally till the reaction was finished. Much heat is generated during the reduction, and the material all dissolved except some tin in excess. On cooling, a double compound of tin with the amido compound and some stannous chloride crystallised out. The crystalline mass was thrown on a filter and all the liquid drawn off as far as possible by means of a filter-pump. The double

compound may be broken up and the tin removed by continued boiling with water. A better method of removing the tin consists in treating the compound with a solution of sodium carbonate. This forms a salt with the amido acid, and throws down the tin as stannous hydroxide, a white flocculent precipitate. On filtering and adding concentrated hydrochloric acid to the solution, the free amido acid is deposited in characteristic colorless rhombic crystals.

Preparation of the diazo compound.—The amido acid is easily converted into the diazo compound by suspending it in very finely powdered condition in absolute alcohol and conducting the oxides of nitrogen into the liquid, taking care to keep it cool by ice water. The success of the operation depends largely upon having the amido acid in the form of the finest powder. When the conversion is complete the granular diazo compound falls rapidly to the bottom of the liquid if the flask is shaken, whereas, as long as there is any amido acid left unchanged it remains suspended in the alcohol for a time, giving it a turbid appearance.

Preparation of the hydrazine compound.—Various methods were tried for the preparation, but that of Strecker and Römer[1] was found to give the most satisfactory results. The details of the operation are as follows :

A solution of 2.7 parts by weight of ordinary crystallised sodium carbonate in 5 parts by weight of water is saturated with sulphur dioxide, and this solution then rendered alkaline with sodium hydroxide. 100 grams of the diazo compound are gradually added to 500 cc. of the cold solution of sulphite. It turns yellow, and, after a considerable amount of the diazo compound has been added, it becomes reddish yellow. After the solution has been heated nearly to boiling for about an hour, 500 cc. more of the sulphite solution are added, and the hydrazine compound then precipitated by means of ordinary concentrated hydrochloric acid. Even while the solution is hot the hydrazine compound separates, and at the same time the solution turns yellow. On adding an excess of hydrochloric acid and allowing the mixture to cool, it solidifies to a mass of crystals. The liquid portion was drawn off by means of a filter pump, the substance washed with water and dried in the air. The substance thus obtained is the free hydrazine compound.

Hydrazine-ortho-toluene-sulphonic acid, $C_6H_3 \begin{cases} CH_3 \\ SO_3H \\ NH-NH_2 \end{cases}$,
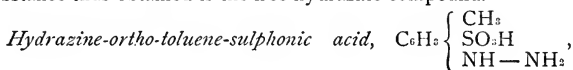
[1] Berichte der deutsch. chem. Gesell. **4**, 784.

crystallises in lustrous scales or plates containing no water of crystal-
lisation. It is difficultly soluble in cold water, more readily in hot
water, and can be purified by crystallisation from water. It acts
like an acid, dissolving in alkalies and being precipitated from the
solutions by acids. It is soluble in hot concentrated sulphuric acid,
but crystallises only on cooling. It has no definite melting point,
but decomposes at $273°-274°$ (uncorr.) and then melts.

Two estimations of nitrogen and one of sulphur were made, the
former by decomposing a weighed quantity of the compound with
a 10 per cent. solution of copper sulphate and collecting and
measuring the gas evolved, the latter by Liebig's method.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3H\\NH-NH_2.\end{cases}$	Found.		
		I.	II.	III.
N	13.86	13.39	13.58	...
S	15.84	...	...	15.74.

An attempt was made to prepare the picric acid compound by
treating the compound with picric acid and ether. On shaking
the hydrazine compound with picric acid and ether, a solution
was obtained. When the ether was allowed to evaporate, a
residue was left which dissolved in hot water, and on cooling,
a flocculent yellow substance separated. A crystallised com-
pound could not be obtained.

Attempts to prepare crystallised barium and calcium salts of the
hydrazine compound were unsuccessful. Both these salts are
easily soluble in water and ordinary alcohol, and insoluble in
absolute alcohol. Efforts to obtain ethers were equally unsatis-
factory. Both when the hydrazine compound was suspended in
absolute alcohol and hydrochloric acid gas passed in, and when it
was boiled with concentrated sulphuric acid and absolute alcohol
with a return condenser, the hydrazine compound appeared to
remain unchanged.

Decomposition of the hydrazine compound with copper sulphate.
—In decomposing the hydrazine compound the directions of
Haller were followed. It was added to a ten per cent. solution of
copper sulphate, which was then boiled. The reaction takes place
without difficulty, and it can be followed by observing the evolution
of nitrogen. In order to be sure that all the hydrazine compound
has been transformed after all evolution of nitrogen has ceased, and
no gas was evolved on adding a few drops more of copper sulphate

solution, enough of the solution was added to color the liquid very slightly blue. The liquid was then filtered from the cuprous oxide, and the filtrate neutralised with chalk. After filtering off the precipitated calcium sulphate, the liquid was evaporated to a small volume, and just enough sodium carbonate added to precipitate the calcium as carbonate. The filtrate, after the removal of the calcium carbonate and calcium sulphate carried down with it, was evaporated to dryness, and the sodium ortho-toluene-sulphonate thus obtained dried on a water-bath. Although the hydrazine compound used was practically pure, the sulphonate formed from it appeared to be far from pure.

By means of the above described reactions there were obtained 655 grams of impure ortho-toluene-sulphonate from 1535 grams of pure para-nitro-toluene.

Oxidation of sodium ortho-toluene-sulphonate.—The salt is oxidised to ortho-sulpho-benzoic acid with considerable difficulty by potassium permanganate in neutral solution. Thus two experiments showed that the oxidation was not complete after twenty-four hours' boiling with an excess of permanganate. If the solution be made alkaline, however, the oxidation is completed in a few hours, yet the greatest difficulty still remains in the separation of the free acid from the products of oxidation in the solution. If hydrochloric acid be added to the solution, the acid salt $C_6H_4 \begin{cases} COOH \\ SO_3K \end{cases}$ is formed, and this has nearly the same solubility as the potassium chloride present. A better method, therefore, is to add a slight excess of sulphuric acid and evaporate nearly to dryness. In this way sulphates, and probably the free acid, are formed. The mixture is treated with 95 per cent. alcohol, which extracts the acid, leaving the greater part of the inorganic salts undissolved. This extract is evaporated and again extracted with alcohol. To this solution barium carbonate is added, the solution filtered, and just enough sulphuric acid added to precipitate the barium. The solution contained the free acid, which crystallised out on evaporation. The yield is extremely small, so that this method is not a practical one.

Formation of benzoic sulphinide from sodium ortho-toluene-sulphonate.—While pure sodium ortho-toluene-sulphonate is converted into toluene-sulphon-amide without difficulty and a good yield is obtained, the salt obtained from nitro-toluene by the

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reactions described above gave a very poor yield of the sulphonamide. The oxidation of the amide was conducted as recommended by Remsen and Fahlberg.[1] We obtained a rather larger yield of the sulphinide than they did, but, on the other hand, we obtained very little of the acid potassium salt, while they obtained the sulphinide and acid salt in equal quantity.

Formation of toluene-sulphon-amide by means of chlorsulphonic acid.—We next tried the method of Claesson and Wallin,[2] which has recently been successfully used by Noyes[3] for the preparation of toluene-sulphon-amide. The method works very well indeed, and is by far the most satisfactory one for the purpose. From a given weight of toluene a better yield is obtained than by any other method, and in less time than is required by other methods.

As it was found by preliminary experiment that the yield in amide by treatment of the chloride prepared by the method of Claesson and Wallin was not as was expected, attempts were made to determine the best conditions for effecting the transformation. The best results were obtained by mixing the chloride with the necessary quantity of ammonium carbonate. From five grams of the chloride three grams of amide were obtained. Besides the pure ortho-sulphon-amide and some of the para-amide, a mixture of the two, melting at 108°–120°, was obtained, and this could not be separated into its constituents. It was thought possible that the ortho-amide contained in the mixture might be obtained by treating with potassium bichromate, as Remsen has shown that the ortho-amide is oxidised with difficulty by this agent, while the para-amide is easily converted into para-sulphamine-benzoic acid. Although, after boiling for several hours with the oxidising mixture, a residue of pure ortho-amide was obtained, this was so small that it was evident that a considerable portion of the ortho as well as all of the para-amide had been destroyed. From fifteen grams of the mixture used, which, as was afterwards shown, consisted of nearly equal parts of the two amides, only three grams of the ortho-amide were recovered.

A better way to effect the separation was found to be the following : It is oxidised by means of potassium permanganate. After having evaporated the solution containing the products of oxida-

tion, nearly neutralised with hydrochloric acid, to about one-fifth its original, it is made very slightly acid and allowed to cool. In this way nearly all the para-sulpho-benzoic acid is separated from the solution and none of the sulphinide is thrown down. After filtering, strong hydrochloric acid is added, and the sulphinide then separates in its characteristic form. This indicates that the sulphinide forms a salt with alkalies which is not decomposed by dilute hydrochloric acid, while the salt of para-sulphamine-benzoic acid is more easily decomposed. The mixture of amides melting at $105°-120°$ when oxidised, and the products separated in this way, gave about equal quantities of sulphinide and para-sulphamine-benzoic acid.

Formation of ortho-sulpho-benzoic acid from benzoic sulphinide.—Benzoic sulphinide may be converted into o-sulpho-benzoic acid : (1) by boiling with barium hydroxide ; (2) by heating in a closed tube with concentrated hydrochloric acid ; or (3) by evaporating on the water-bath with hydrochloric acid. The last method is the most convenient. The sulphinide is heated with concentrated hydrochloric acid on the water-bath for two days, the acid being from time to time renewed. Finally it is evaporated to dryness, and the residue dissolved in a small quantity of water. If the sulphinide contains any para-sulphamine-benzoic acid, as is generally the case, this is left undissolved, and most of the ammonium chloride crystallises out on standing. By slow evaporation the mother liquor deposits large colorless crystals of the free acid.

The acid is soluble in about two parts of cold water, very difficultly soluble in absolute alcohol, and almost completely insoluble in ether. It does not melt under $250°$, but considerably above that it melts, at first apparently without change, and then with slight sublimation of a very deliquescent crystalline substance, possibly the anhydride.

A determination of sulphur made by Mr. A. F. Linn gave the following results :

0.1358 gram substance gave 0.1555 gram $BaSO_4 = 15.72$ per cent. S.

Calculated for the formula $C_6H_4 \begin{cases} COOH \\ SO_2OH \end{cases} = 15.84$ per cent. S.
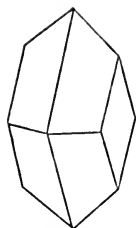
A crystallographic examination of the acid showed it to belong to the orthorhombic system. Axial ratio, $a : b : c = 0.5507 : 1 : 0.8121$; Planes, P and $\infty P \infty$;

Angles measured. $\left\{ P : P \left\{ \begin{array}{l} \text{edge } x = 131^\circ\ 5' \\ \text{``}\quad y = 82^\circ\ 18' \\ \text{``}\quad z = 118^\circ\ 40' \end{array} \right. \right.$
$\left. P : \infty P \infty = 114^\circ\ 38' \right.$

The crystals are up to 8 mm. in length. The pyramidal faces are generally etched, so that the image is poor.

INVESTIGATIONS ON THE SULPHINIDES.

VI.—ON THE ETHERS OF BENZOIC SULPHINIDE.[1]

By R. N. Brackett.

Methyl Ether of Benzoic Sulphinide.—This was prepared by treating the silver salt as well as the potassium salt of benzoic sulphinide with methyl iodide in a sealed bottle placed in a water-bath. The heating was continued for about two hours. Action takes place rapidly with the formation of silver iodide, and appears to be complete in about half an hour. After cooling, absolute alcohol is added, and the excess of methyl iodide boiled off on a water-bath. The silver iodide is then filtered off and washed with absolute alcohol. On evaporating the filtrate to a small volume and allowing to cool, crystals separate. On recrystallising these from water they melt at 131°–132°, and this does not change after repeated recrystallisations. The compound crystallises in long, flat needles. It is easily soluble in anhydrous ether, in absolute alcohol and in hot water, but difficultly soluble in cold water. It can easily be purified by crystallising from water. Three determinations of sulphur gave the following results:

I. 0.18425 gram substance gave 0.21775 gram BaSO₄.
II. 0.1690 gram substance gave 0.1984 gram BaSO₄.
III. 0.33385 gram substance gave 0.3985 gram BaSO₄.

	Calculated for $C_6H_4 \left\{ \begin{smallmatrix} CO \\ SO_2 \end{smallmatrix} \right\} NCH_3$.	I.	Found. II.	III.
S	16.24	16.23	16.13	16.39

[1] Communicated by Ira Remsen.

Ethyl Ether of Benzoic Sulphinide.—Since the experiments described in this paper were completed, a paper by Fahlberg and List has appeared,[1] in which the ethyl ether of benzoic sulphinide, obtained by treating the sodium salt with ethyl iodide, is described. When the silver salt of the sulphinide is treated with ethyl iodide, two well crystallised products are obtained. Both crystallise in sharp, slender radiating needles. One melts at 83°–84° and the other at 96°–97°. Judging by the results obtained by Fahlberg and List, it would appear that the substance melting at the lower point is the ethyl ether of ortho-sulphamine-benzoic acid, while that melting at the higher point is the ether of the sulphinide, though Fahlberg and List give the melting point of the latter at 93°–94°, which is a little lower than I found it. The ether of ortho-sulphamine-benzoic acid could hardly have been formed in the reaction in the pressure bottle, as dry ethyl iodide and dry silver salt were used. It must have been formed in the process of purification, unless, indeed, the silver salt used was a mixture of the salts of the sulphinide and of the acid.

Propyl Ether of Benzoic Sulphinide.—This was prepared from the silver salt. The yield was not good. The product crystallised very much as the other ethers, and melted at 60°–70°.

Action of Phosphorus Pentachloride and Methyl Alcohol on Benzoic Sulphinide.—When benzoic sulphinide is mixed with an equal weight of phosphorus pentachloride and the mixture heated at 90° to 100° in a water-bath, hydrochloric acid is given off, and the mass gradually becomes semi-fluid. On cooling it does not all solidify. If the flask in which the operation is conducted be surrounded by cold water, and methyl alcohol added, hydrochloric acid is given off, much heat is generated, and a crystalline product separates. When the crystalline product is boiled with methyl alcohol it gradually dissolves. The liquid is then evaporated to a small volume, and, on cooling, crystals separate which, recrystallised from water, do not melt at 330°. From the mother liquor a small quantity of a crystalline substance melting at 123°–125° was obtained. The latter is the substance obtained by Remsen and Palmer.[2] The former is an acid, showing an acid reaction toward litmus paper in aqueous solution, and being soluble in alkalies and reprecipitated by mineral acids. The barium and calcium salts of this acid were made. They are crystallised

[1] Berichte der deutsch. chem. Gesell. **20,** 1596.   [2] This Journal **8,** 226.

compounds, easily soluble in water. An analysis of the calcium
salt showed it to contain 7.91 per cent. water and 8.95 per cent.
calcium. It was not further studied.

The compound melting at 123°–125° can be prepared in pure
condition, and the reaction is a fairly clean one if care is taken to
regulate the temperature in all the operations involved. The best
result was obtained in the following way: 5 grams of benzoic
sulphinide and an equal weight of phosphorus pentachloride were
placed in a small Erlenmeyer flask, fitted with a cork through
which passed a long glass tube. The flask was heated in a water-
bath at 70°–75°. The reaction began between 65° and 70°. The
heating was continued for two hours, when the mass became semi-
fluid and all evolution of hydrochloric acid ceased. On cooling,
all did not solidify. The flask was then surrounded with a freezing
mixture of crushed ice and hydrochloric acid, and methyl alcohol
gradually added from a drop-funnel. When the addition of a little
methyl alcohol ceased to produce an evolution of hydrochloric
acid gas, the crystalline product which had separated was boiled
with methyl alcohol. The flask was then surrounded with a freez-
ing mixture, and crystals were deposited which melted at 123°–125°.
After several recrystallisations from water, the melting point rose
to 125°–126° and did not change after that. If the operations are
conducted as described, a good yield of this substance is obtained,
and none of the substance with the high melting point.

The substance melting at 125°–126° crystallises in radiating
needles. It is easily soluble in alcohol, ether, and hot water. It
is difficultly soluble in cold water, and can easily be purified by
recrystallisation from water. Determinations of sulphur and of
nitrogen gave the following results :

I. 0.2939 gram substance gave 0.2989 gram BaSO₄.

II. 0.1000 gram substance gave 0.1007 gram BaSO₄.

By Kjeldahl's method, 0.12225 gram substance gave an
amount of ammonia corresponding to 5.74 per cent. N.

That the substance has not the composition of a simple ether of
benzoic sulphinide is shown by a comparison of the figures :

	Calculated for $C_6H_4{<}{CO \atop SO_2}{>}NCH_3$.	Found.	
		I.	II.
S	16.24	13.87	13.83
N	7.11	5.74	...

On the other hand, a substance of the composition

$C_6H_4{<}^{C(OCH_3)_2}_{SO_2}{>}NH$ requires 13.97 per cent. sulphur and 6.11 per cent. nitrogen, figures which agree fairly well with those obtained in the analyses. From this it would appear that benzoic sulphinide has the constitution represented by the formula

$C_6H_4{<}^{CO}_{SO_2}{>}NH$, and that when phosphorus pentachloride acts upon it, the carbonyl oxygen is replaced by two chlorine atoms, forming a chloride of the formula $C_6H_4{<}^{CCl_2}_{SO_2}{>}NH$. By the action of methyl alcohol both the chlorine atoms are replaced by methoxy groups and the compound $C_6H_4{<}^{C(OCH_3)_2}_{SO_2}{>}NH$ formed.

A compound analogous to this was obtained by Stokes[1] by treating phthalic sulphinide successively with phosphorus pentachloride and methyl alcohol. The chloride obtained in this case had the composition represented by the formula

$C_6H_3\begin{Bmatrix}SO_2\\CCl_2\\COCl\end{Bmatrix}N.POCl_2$, and the ether that represented by the

formula $C_6H_3\begin{Bmatrix}SO_2\\C(OCH_3)_2\\COOCH_3\end{Bmatrix}NH$.

When the dimethyl-ether of benzoic sulphinide is boiled with water and barium carbonate, it forms a salt which proved to be the barium salt of the sulphinide. It crystallises in needles of a silky appearance, is easily soluble in water, and has the characteristic sweet taste of the salts of the sulphinide. An analysis of the air-dried salt gave 12.89 per cent. water and 23.42 per cent. barium.

	Calculated for $\left[C_6H_4\{{}^{CO}_{SO_2}{>}N\right]_2Ba+4H_2O.$	Found.
Ba	23.91	23.42
4H_2O	12.57	12.89

That this is really the salt of the sulphinide is shown by the fact that the sulphinide separates from it when it is treated with hydrochloric acid.

Chloride of Benzoic Sulphinide.—When the semi-fluid mass formed by the action of phosphorus pentachloride on benzoic

[1] This Journal **6**, 275.

sulphinide is cooled down with a freezing mixture, a crystalline product separates on the addition of methyl alcohol. In one experiment this crystalline product was filtered off without first boiling it with methyl alcohol. On boiling it with water to recrystallize it, the sulphinide was obtained and no methyl compound. This was probably the chloride. On preparing some of it in the way described, it was found to contain chlorine. An attempt was made to recrystallise it from petroleum ether, but it is very slightly soluble. After boiling with petroleum ether the compound was sweet, though it still contained chlorine. Fearing, however, that some decomposition had taken place, no analysis was made. In another experiment, anhydrous ether was used for the purpose of isolating the chloride. The crystalline product was carefully washed repeatedly with anhydrous ether to remove all the phosphorus oxychloride, and then placed over calcium chloride in a desiccator. Determinations of chlorine gave varying results, and none that agreed with those required by the formula $C_6H_4\left\{{CCl_2\atop SO_2}\right>N.POCl_2$. Lack of time and material prevented a further examination of the substance.

The facts brought to light in this investigation speak in favor of the formula $C_6H_4\left\{{CO\atop SO_2}\right>NH$ for benzoic sulphinide. Further, the evidence furnished by the work of Fahlberg and List[1] is also in favor of the same formula.

P-AMIDO-*O*-SULPHO-BENZOIC ACID.

By W. A. HEDRICK.

Of the ten isomeric substances of the formula $C_6H_3\left\{{NH_2\atop SO_3H\atop CO_2H}\right.$, four, or perhaps five, are known. The first one was described by Limpricht and Uslar.[2] They obtained it by treating *m*-sulphobenzoic acid with nitric acid and sulphuric acid, and reducing the nitro acid with hydrogen sulphide. By heating *m*-amido-benzoic acid

[1] Loc. cit.　　　　　　　　　　[2] Annalen der Chemie **106**, 79.

with sulphuric acid, Griess[1] obtained two acids which can be separated by means of the barium salts. By reducing *m*-nitro-*p*-sulpho-benzoic acid, Hart[2] obtained the corresponding amido acid. This is probably identical with one of the acids described by Griess. Hart also made *o*-amido-*p*-sulpho-benzoic acid and *p*-amido-*o*-sulpho-benzoic acid from the corresponding nitro-compounds. In the course of some other investigations the preparation of this last acid became necessary, and I therefore undertook a study of the best conditions for its preparation, as well as of the acid itself and some of its derivatives.

Preparation.—The potassium salt of *p*-nitro-*o*-toluene-sulphonic acid was first made, and this subjected to oxidation by means of potassium permanganate. The best proportions are as follows: Ten parts potassium salt, 3 parts potassium hydroxide, 22 parts permanganate, and 500 parts water. The permanganate and hydroxide are dissolved in the requisite quantity of water and the salt added. The whole is then heated in a water-bath with occasional shaking, until the permanganate is completely reduced and the liquid has a yellow color. The precipitated oxides of manganese are filtered off, the solution nearly neutralised with hydrochloric acid, and evaporated until a portion nearly solidifies when treated with hydrochloric acid. The whole solution is then acidified and, after cooling, filtered. The precipitate thus obtained is the acid potassium salt of *p*-nitro-*o*-sulpho-benzoic acid,

$$C_6H_3 \begin{cases} COOH\ (1) \\ SO_2OK(2). \\ NO_2\ \ \ (4) \end{cases}$$ There is some loss in this process, but the yield

is fairly good.

The nitro-compound is best reduced by dissolving the acid potassium salt in dilute ammonia and, while keeping the solution gently warmed, passing in hydrogen sulphide. A little ammonia is added from time to time, but a large excess must be avoided. During the reduction the solution changes color. The solution is filtered from precipitated sulphur, evaporated to dryness, the residue dissolved in water and acidified with hydrochloric acid. The amido acid is then precipitated in semi-crystalline form. It is further purified by dissolving in a dilute solution of sodium carbonate, again filtering and precipitating. It is then recrystallised

[1] Journal für prak. Chemie [2], **5**, 244.　　　　[2] This Journal **1**, 340.

from water. As regards the yield of the pure acid, it was found to be about half the weight of the nitro-toluene used.

Salts of the Amido Acid.—The only salts of the acid mentioned by Hart are the ammonium and neutral barium salts. To obtain the barium salt, ten grams of the amido acid were boiled in a flask with barium carbonate. A soluble salt was first formed, but on continued boiling in the presence of barium carbonate, an insoluble compound is formed. Believing that the salt had become dehydrated by boiling, a part of the precipitate was transferred to a large flask, a large quantity of water added, and the contents boiled for an hour. The solution was then filtered, but only very little had passed into solution. To obtain the soluble salt the boiling was stopped, and the excess of barium carbonate filtered off before the insoluble salt was formed.

Acid Barium Salt.—This salt, made as indicated above, separated from the solution on cooling. The crystals were small columns; they are quite easily soluble in hot water, but much less in cold water. They are insoluble in alcohol, and blacken slightly on long exposure to light and air. No definite results could be obtained in determining the water of crystallisation, but judging by the percentage of barium found, the composition of the crystals

is represented by the formula $\left[C_6H_3 \begin{cases} NH_2 \\ SO_3 \\ CO_2H \end{cases} \right]_2 Ba + 5H_2O.$

I. 0.3170 gram salt gave 0.1130 gram $BaSO_4$.

II. 0.2537 gram salt gave 0.0909 gram $BaSO_4$.

	Calculated for $(C_6H_3.NH_2.CO_2H.SO_3)_2Ba + 5H_2O.$	Found.	
		I.	II.
Ba	20.92	20.96	21.07

The difficulty in determining the water of crystallisation was due to the fact that the salt is comparatively easily decomposed by heat.

Lead Salt.—The lead salt was prepared, but it could not be obtained in pure condition. The analysis gave the following results :

I. 0.4349 gram salt gave 0.3199 gram $PbSO_4$.

II. 0.3542 gram salt gave 0.2603 gram $PbSO_4$.

	Calculated for $(C_6H_3.NH_2.CO_2.SO_3)Pb.$	Found.	
		I.	II.
Pb	48.96	50.25	50.23

The neutral ammonium salt was made by dissolving the acid in

a small quantity of ammonia and evaporating to dryness on a water-bath. It was hoped that from this the lead, zinc and magnesium salts might be obtained by double decomposition with lead acetate, zinc and magnesium sulphates. But nothing was precipitated, nor did the salts crystallise out on evaporating to a small volume.

Silver Salt.—By adding silver nitrate to the solution of the neutral ammonium salt a precipitate is formed. This is a white powder, practically insoluble in hot and cold water, but decomposed by nitric acid. The analyses gave the following results:

I. 0.4264 gram salt gave 0.2786 gram AgCl.

II. 0.2854 gram salt gave 0.1865 gram AgCl.

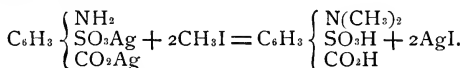|	Calculated for $C_6H_3.NH_2.CO_2Ag.SO_3Ag$.	I.	Found. II.
Ag	50.11	49.19	49.24

Methyl-amido-sulpho-benzoic Acid.—The silver salt of amido-sulpho-benzoic acid was treated with methyl iodide and methyl alcohol in a closed vessel at the temperature of the water-bath. After expelling the excess of the liquid reagents, the residue was immediately boiled with water. The solution thus obtained had a dark color, which was only partially removed by boiling with animal charcoal. It was boiled with finely powdered calc spar and filtered. On standing for some time, small crystalline particles were deposited. These were separated and further purified by crystallisation. They are not easily soluble, were of a dark color, and do not appear homogeneous. The results of the analyses are as follows:

I. 0.1284 gram salt gave 0.0626 $CaSO_4$.

II. 0.1953 gram salt gave 0.0936 $CaSO_4$.

	Calculated for $C_6H_3 \begin{cases} N(CH_3)_2 \\ CO_2 \\ SO_3 \end{cases} Ca$.	I.	Found. II.
Ca	14.13	14.34	14.38

The reaction between the silver salt and methyl iodide may be represented thus:

$$C_6H_3 \begin{cases} NH_2 \\ SO_3Ag \\ CO_2Ag \end{cases} + 2CH_3I = C_6H_3 \begin{cases} N(CH_3)_2 \\ SO_3H \\ CO_2H \end{cases} + 2AgI.$$

With ethyl iodide the silver salt appears to act differently. The product obtained, which consisted of a gummy mass, was boiled

with water and barium carbonate. On cooling, a white crystalline substance was deposited. This could easily be recrystallised from water. The analysis gave the following results:

0.1630 gram salt gave 0.0605 gram $BaSO_4$.

	Calculated for $(C_6H_3.NHC_2H_5.CO_2H.SO_3)_2Ba$ or $(C_6H_3.NH_2.CO_2C_2H_5.SO_3)_2Ba.$	Found.
Ca	21.82	21.92

As the salt appeared to be neutral, the formula

$$\left[C_6H_3 \left\{ \begin{matrix} NH_2 \\ CO_2C_2H_5 \\ SO_3 \end{matrix} \right. \right]_2 Ba \text{ is the more probable.}$$
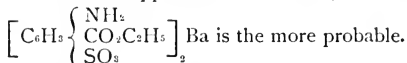
Attempts to prepare Acetyl and Benzoyl Compounds of the Amido Acid.—The amido acid was heated for about two hours with acetic anhydride in a flask connected with an inverted condenser. On getting rid of the acetic acid it was found that no action had taken place, the original acid being obtained unchanged, as was shown by its solubility and the properties of the soluble barium salt. Further, the crystallised barium salt was analysed, with the following results:

I. 0.2172 gram salt gave 0.0776 gram $BaSO_4$.

II. 0.2675 gram salt gave 0.0945 gram $BaSO_4$.

	Calculated for $\left[C_6H_3 \left\{ \begin{matrix} NH_2 \\ SO_3 \\ CO_2H \end{matrix} \right. \right]_2 Ba + 5H_2O.$	Found.	
		I.	II.
Ba	20.92	21.01	20.80

The neutral barium salt was made also by adding barium chloride to a solution of the neutral ammonium salt. It was analysed with the following results:

I. 0.1915 gram salt lost 0.086 gram H_2O and gave 0.1205 gram $BaSO_4$.

II. 0.1062 gram salt lost 0.047 gram H_2O and gave 0.067 gram $BaSO_4$.

	Calculated for $C_6H_3 \left\{ \begin{matrix} NH_2 \\ SO_2 \\ CO_2 \end{matrix} \right\} Ba + H_2O.$	Found.	
		I.	II.
Ba	36.98	37.00	37.09
H_2O	4.87	4.5	4.43

A portion of the acid was heated with benzoyl chloride in an oil-bath to 150° for three hours. At no time was the evolution of any considerable quantity of hydrochloric acid noticed. On getting rid of the benzoyl chloride, nothing but the unchanged amido acid was obtained.

In this case the basic properties of the ammonia residue are entirely destroyed by the presence of the sulphonic acid group in the ortho position, and the nitro group in the para position.

Diazo Compound.—The diazo compound corresponding to *p*-amido-*o*-sulpho-benzoic acid is mentioned by Remsen and Palmer,[1] but they give no directions for preparing it, nor do they describe it. Three methods were tried. First, the amido acid was suspended in water kept cold by surrounding it with ice, and the oxides of nitrogen conducted into the liquid. After some time the liquid was filtered off and examined, but there was practically nothing in solution. The solid portion exploded when gently heated, and decomposed with an evolution of nitrogen when boiled with water, but it did not decompose with alcohol. Second, the ammonium salt of the amido acid was made, and nitrous acid fumes conducted into the solution. It changed color, and in about half an hour a crystalline substance was deposited. This was filtered, washed and dried, and was shown to be the diazo compound. The best way to prepare the diazo compound, however, is to conduct nitrous fumes into an aqueous solution of the acid barium salt of the amido acid in which some of the salt is suspended. Generally, in the course of about twenty minutes a white crystalline homogeneous mass is deposited. This is whiter than the diazo compound prepared in the other ways. The nitrogen in the diazo compound prepared from the ammonium salt, and in that from the barium salt, was determined by boiling with water in an atmosphere of carbon dioxide and collecting the gas over caustic alkali. Determinations I and II were made with the compound from the barium salt; determination III with the compound from the ammonium salt.

I. 0.6999 gram compound gave 74.32 cc. N at 17.8° and 764.8 mm.

II. 0.5963 gram compound gave 64.58 cc. N at 20° and 758.8 mm.

III. 0.4826 gram compound gave 48.41 cc. N at 20° and 758.7 mm.

	Calculated for $C_6H_3\begin{Bmatrix} N_2 \\ SO_3 \\ CO_2H \end{Bmatrix}>$	I.	Found. II.	III.
N	12.28	12.31	12.24	11.42.

Hydroxy-sulpho-benzoic Acid, $C_6H_2\begin{Bmatrix} CO_2H \\ SO_3H\ (o) \\ OH\quad (p) \end{Bmatrix}$—This acid was

[1] This Journal **8,** 251.

prepared by boiling the diazo compound with water. On evaporating to dryness, a red gummy mass was obtained. A concentrated solution was placed under a bell jar over sulphuric acid and allowed to evaporate spontaneously. Impure crystals were obtained. These deliquesced when exposed to the air. To the concentrated aqueous solution of the acid, alcohol and ether were added successively, but nothing was precipitated.

Barium Hydroxy-sulpho-benzoate, $\left[C_6H_3 \left\{ \begin{array}{l} OH \\ SO_3 \\ CO_2H \end{array} \right\} \right]_2 Ba.$ — This

salt was prepared by boiling the aqueous solution of the acid with barium carbonate. A soluble salt was formed at first, but by continued boiling with barium carbonate an insoluble salt was formed. This insoluble salt is insoluble in an excess of the hydroxy acid, and in dilute acetic acid, but soluble in dilute hydrochloric acid. When the solution of the soluble salt is evaporated to a small volume it does not deposit crystals, but the salt separates in the form of a powder. The analyses gave the following results :

I. 0.2506 gram salt gave 0.0894 gram $BaSO_4$.

II. 0.2048 gram salt gave 0.0753 gram $BaSO_4$.

	Calculated for $\left[C_6H_3 \left\{ \begin{array}{l} OH \\ SO_3 \\ CO_2H \end{array} \right\} \right]_2 Ba.$	Found. I.	II.
Ba	23.97	22.02	22.76

The neutral barium salt was made by adding barium chloride to a solution of the neutral ammonium salt. The analyses gave the following results :

I. 0.6230 gram salt gave 0.5178 gram $BaSO_4$.

II. 0.4898 gram salt gave 0.4062 gram $BaSO_4$.

	Calculated for $\left[C_6H_3 \left\{ \begin{array}{l} O \\ SO_3 \\ CO_2 \end{array} \right\} \right]_2 Ba_3.$	Found. I.	II.
Ba	48.80	48.80	48.76

Calcium Hydroxy-sulpho-benzoate, $C_6H_3 \left\{ \begin{array}{l} OH \\ CO_2 \\ SO_3 \end{array} \right.\!\!\!\!> Ca + 5H_2O.$

—The calcium salt was prepared by boiling the aqueous solution of the acid with finely powdered calcium carbonate. It is fairly easily soluble in hot water, but less in cold. It crystallises in beautiful columns, though sometimes radiating masses were obtained. The analyses gave the following results :

I. 0.3947 gram salt lost 0.1026 gram H_2O and gave 0.1548 gram $CaSO_4$.

II. 0.3187 gram salt lost 0.0799 gram H_2O and gave 0.1250 gram $CaSO_4$.

	Calculated for $C_6H_3\begin{Bmatrix} OH \\ CO_2 \\ SO_3 \end{Bmatrix} > Ca + 5H_2O.$	I.	Found. II.
Ca	11.57	11.58	11.53
H_2O	26.01	26.00	25.75

The water is not driven off under about 185°.

Mr. A. C. Gill, a student in mineralogy in this university, has kindly furnished me with the following information regarding the crystals of the salt:

" The crystals are triclinic, elongated in the direction of the vertical axis.

" Axial ratio ă : b̄ : c′ = 0.9567 : 1 : 1.0121.

" The angles obtained by taking the mean of the measurements of several crystals are as follows :

$$\infty P \,\bar{\infty} \wedge \infty P \,\bar{\infty} = 129° \; 11'$$
$$\infty P \,\bar{\infty} \wedge oP = 134° \; 25'$$
$$\infty P \,\bar{\infty} \wedge oP = 140° \; 52'$$
$$P \,\bar{\infty} \wedge oP = 115° \; 14'$$
$$\infty P \,\bar{\infty} \wedge \infty P = 110° \; 32'$$

" Though the crystals are quite brittle, no definite cleavage could be determined. The rounding of the faces on most of the crystals gave a large variation in the angles, but the more perfect faces gave agreeing results."

Hydrazine Compound.—To prepare the hydrazine compound, the diazo compound was added to a cold saturated solution of neutral sodium sulphite. At first the solution turned reddish yellow, and then became golden yellow. When the diazo compound had completely dissolved, the solution was boiled and hydrochloric acid was added. Soon a crystalline deposit was formed. The yield was fairly good. The hydrazine compound obtained in this way crystallises in small white needles which are not very soluble in cold, but more readily in hot water, from which
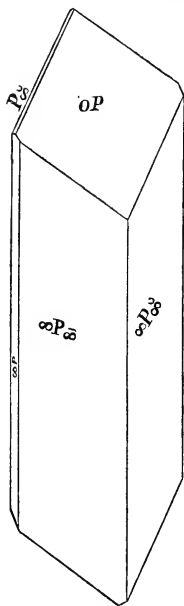
it crystallises on cooling. It readily reduces copper and silver salt solutions.

A small quantity was boiled with a dilute solution of copper sulphate and a substance which had the general properties of ortho-sulpho-benzoic acid was obtained, though other substances were formed at the same time.

The hydrazine compound has acid properties, and when its solution is boiled with barium carbonate, a soluble barium salt is formed, which is deposited from the solution in the form of sharp pointed needles.

The work described above was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

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XIV. — A CONVENIENT FORM OF GAS RECEIVER FOR USE IN GAS ANALYSIS BY THE ABSORBIOMETRIC METHOD.

By Francis A. Wilber.

In following out the method for determining dissolved gases, in the analysis of potable water, as given by Prof. J. W. Mallet in his report to the National Board of Health,[1] difficulty was experienced in handling the gases after they were collected. Prof. Mallet used for this purpose a Cooper's receiver, see Fig. 1, with a modified form of stopper. The introduction into this receiver of the absorbent solutions was attended with some trouble, and to obviate this, the receiver described below, Fig. 2, was devised.

This receiver consists of two parts, A and B, connected by the rubber tube T. The part A is divided into two parts by the large and accurately ground stop-cock C. The upper portion D is graduated from C upward into one-tenth cc. It is used to contain the absorbent solutions while they are being introduced into the lower portion E. E is graduated, from C downward, into one-tenth cc. The receiver has a capacity of 50 cc. The two

[1] Report of National Board of Health for 1882, pp. 284–286.

Fig. 1.

Fig. 2.

A

B
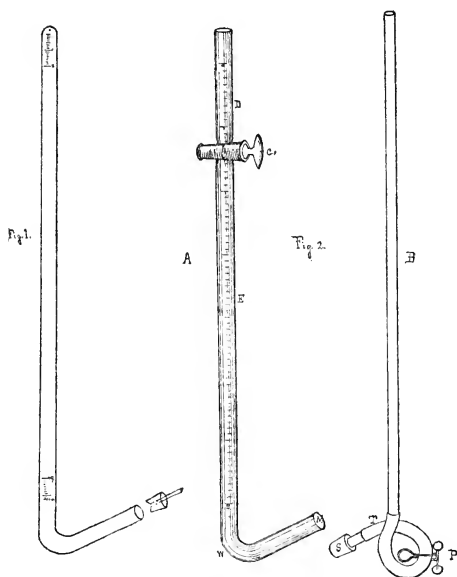
parts *A* and *B* are supported in clamps in a vertical position ; *E* is completely filled with mercury before it is brought into position. A sheet-iron pan is put beneath them to catch the overflow of mercury. The mixture of gases to be analysed is then introduced into *E ;* the tip of the tube, which delivers the gases, being thrust through the mouth *M* until it touches the wall of the receiver at *W.* After the gases are introduced the stopper *S* is forced tightly into *M,* and mercury is poured into *B,* the pinch-cock *P* being open until the level of mercury is the same in *E* and *B.* The volume of the enclosed gases is then read and temperature and pressure noted. The pinch-cock is now shut, the stopper *S* removed from *M,* and the first absorption made. In water analyses, where oxygen, carbonic acid and nitrogen are the gases determined, the absorbent solutions are caustic soda for carbonic acid and alkaline solution of pyrogallol for oxygen. The residual gas is taken for nitrogen. The caustic soda solution used had a specific

31

gravity of 1.05, as recommended by Weil and Zeitler,[1] and 10 cc. were used for each absorption.

It is put in D, the cock C cautiously opened a little, and the solution allowed to run slowly down. Absorption takes place rapidly as the gases are washed by the flowing solution. With care the absorbent can be run in to the last one-tenth cc. without danger of admitting air. After admitting the caustic soda, S is replaced in M, P is opened, and the mercury in B brought to the proper level. This level is one-thirteenth of the distance occupied by the caustic soda in E above the mercury level of E. Any air under S is allowed to escape through B before the level is made, and after standing 15–20 minutes the reading is taken, and thermometer and barometer read. P is again closed, S removed from M, and the solution of pyrogallol is quickly introduced into the receiver. The charge used for oxygen absorption is 0.5 gram solid pyrogallol dissolved in 10 cc. of the above-mentioned caustic soda solution. It is exposed to the air as short a time as possible.

After this is introduced, S is replaced in M, P opened, the mercury in B brought to its proper level, and a third reading taken. From these three readings, when corrected for temperature and pressure, the oxygen, carbonic acid, and nitrogen are determined. Excellent results were obtained with the receiver when samples of atmospheric air were analysed.

The labor demanded in making such absorptions in gas analysis is much reduced by the use of this receiver. It will be found to be a simple and easily managed form of apparatus for rapid work.[2]

New Brunswick, N. J., *July* 16, 1887.

1 Liebig's Annalen **205**, 255.

2 The apparatus may be obtained of Emil Greiner, 79 Nassau Street, New York.

V.—ON THE CHEMISTRY OF FISH.

Part I.—ANALYSES OF SPECIMENS OF AMERICAN FISHES.

By W. O. Atwater.

The Commissioner's Reports of the United States Commission of Fish and Fisheries for 1880 (Washington, 1883) and 1883 (Washington, 1885) have contained accounts of the progress of an investigation of the chemical composition and nutritive values of American food-fishes and invertebrates. A monograph including detailed results of this research up to the present date is now in preparation, and, it is expected, will be published by the Commission. Awaiting this monograph, the present article and others which may follow are intended to epitomise some of the principal results.

The investigation in its present status includes :

I. Chemical analyses of the flesh of American food-fishes and invertebrates.

II. Experiments upon the digestibility of the flesh of fish.

III. Studies of the chemical constitution of the albuminoids of the flesh of fish.

Analyses have been made of flesh of American fishes, 122 specimens belonging to 52 species ; of flesh of European fishes, 3 specimens of 2 species ; of flesh, etc., of American invertebrates, 64 specimens of 11 species.

Two of the European specimens were of a species included in the American fishes. The total number of specimens of fish analysed is, therefore, 125, belonging to 53 species. These, with the invertebrates, make 189 specimens belonging to 64 species. Since, in numerous cases, analyses were made of more than one part of the specimen, the actual number of analyses is larger than these figures imply.

I am informed by gentlemen connected with the United States Fish Commission that nearly one thousand different species of fish are used for food in the United States. When we consider that almost no other analyses of American food-fishes have been made (I am aware of but two); that different specimens of the same species vary considerably in composition, so that several

analyses of each are necessary to show the ranges of variation and the average composition in the different circumstances of locality, season, size, age, sex, etc.; and that, from both the chemical and economical standpoints, studies of the constitution of the ingredients of the flesh and of other tissues are needed to make our information at all complete, it is evident that the work here reported can be regarded as only the beginning of a much needed research.

Along with these studies, a series of analyses of meats, dairy products, and other food materials, animal and vegetable, have been undertaken at the instance of the United States National Museum, to furnish data for illustrating and explaining its food collections. These analyses, though not specifically a part of the investigation herewith reported, form an important economical supplement to it, because of the desirability of data for comparisons of fish with other foods. The number of analyses of the latter kind already made is about ninety.

While the work has been constantly under my immediate supervision, and much of it has been done by myself, the larger part of the details have been skilfully and faithfully performed by my assistants, Messrs. G. P. Merrill, W. H. Jordan, J. H. Long, Miles Beamer, E. B. Voorhees, E. W. Rockwood, and especially C. D. Woods.

I.—Names and Synonyms of American Fishes Analysed.

Of the specimens of fishes analysed, a considerable number were found in fish markets in Middletown, Conn. These were mostly of common species whose names were well known to us. By far the larger number were supplied through the kindness of Mr. E. G. Blackford, Fish Commissioner of the State of New York, who gave with each specimen the common name and in some cases the Latin name. Specimens with which we were not familiar, or the names of which were for other reasons a matter of doubt, were referred to Prof. W. N. Rice, of this college, who was so kind as to either identify them himself or have them identified under his supervision. Prof. Rice tells me that the specific differences are sometimes difficult to distinguish, especially in specimens that are not entirely normal or have been distorted in packing and transport, so that it is not impossible that errors have been made. I cannot believe, however, that with the literature of the subject and

many typical specimens in the college museum conveniently at hand and freely used, many or serious mistakes could have occurred. Some doubtful cases are indicated in the explanations and tabular statements beyond.

The selection of names and the classification of the specimens has been a perplexing matter, on account of the differences in usage of ichthyologists as to both the generic and specific names which should be applied to a given species, even the same authority insisting on different names for a given species in different writings.

In accordance with the suggestion of my colleagues, Professors Rice and Conn, the names given in Jordan and Gilbert's Synopsis of the Fishes of North America[1] have been adopted, except in a few cases in which other names, generally those employed in previous, have been used.

I am under obligations, not only to the gentlemen named, but also to Prof. D. S. Jordan for assistance in the preparation of the following list of synonyms, which is simply for the convenience of chemists and others to whom the variations in current terminology are perplexing. Where the French and German names of the species which occur in Europe were known to me, they have been inserted.

The order of arrangement here and in some of the principal tabular statements of analyses follows, in the main, that of Jordan and Gilbert.

Sundry matters regarding identification, names, etc., will be spoken of in more detail in the monograph referred to above.

LIST OF NAMES OF FISHES.

Acipenser sturio.   Common sturgeon ; Fr., Esturgeon ; Ger., Stör.   No. 238.

Moxostoma velatum.   Small-mouthed red horse ; Buffalo fish.   No. 258.

Clupea harengus.   Common herring ; Whitebait (young) ; Fr., Hareng ; Ger., Häreng.   Nos. 33, 47.

Clupea pilchardus (?).   Sardine ; Pilchard ; Fr., Sardine ; Ger., Pilchard. No. 87.

Clupea vernalis ; Clupea mattowscea, Günther.   Alewife ; Branch herring ; Gaspereau.   Nos. 5, 220.

Clupea sapidissima.   Common shad.   Nos. 6, 10, 32, 212, 221, 245, 249.

Osmerus mordax ; O. viridescens, Günther.   American smelt.   Nos. 23, 207.

Coregonus clupeiformis ; C. albus, Günther.   Common white fish.   No. 18.

[1] Bulletin of the U. S. National Museum, No. 16.

Coregonus sp. (*tullibee* or *artedi?*). Cisco ; Lake herring. No. 111.

Oncorhyncus chouicha : O. quinnat, Günther. California salmon ; King salmon ; Columbia salmon ; Sacramento salmon ; Chinnook salmon ; Tyee salmon ; Saw-kwey ; Chouica. Nos. 27, 29, 96, 233, 241.

Salmo salar. Common Atlantic salmon ; Fr., Saumon ; Ger., Lachs, Salm. Nos. 14, 77, 78, 279, 280, 35, 36.

Salmo salar subsp. sebago. Land-locked salmon. Nos. 40, 41.

Salvelinus namaycush ; Salmo namaycush, Günther. Lake trout ; Mackinaw trout ; Great lake trout ; Longe (Vermont) ; Togue (Maine). Nos. 17, 255.

Salvelinus fontinalis ; Salmo fontinalis, Günther. Brook trout ; Speckled trout. Nos. 24, 254, 256.

Esox reticulatus. Common eastern pickerel ; Green pike. Nos. 100, 224.

Esox lucius. Pike, Pickerel (Vermont, New York, etc.) ; Fr., Brochet ; Ger., Hecht. No. 98.

Esox nobilior. Mascalonge ; Muskallunge ; Musquallonge ; Maskinonge. No. 45.

Anguilla rostrata ; A. Bostoniensis, Günther. Common eel. Nos. 4, 217.

Mugil albula ; M. lineatus, Günther. Striped mullet. No. 126.

Scomber scombrus ; Scomber scomber, Günther. Common mackerel ; Fr., Macquereau vulgaire ; Ger., Makrele. Nos. 8, 13, 30, 39, 42, 94, 95, 219, 230, 261.

Cybium maculatum, Günther ; *Scomberomorus maculatus,* Jor. and Gil. Spanish mackerel. No. 43.

Trachynotus carolinus ; T. pampanus, Günther. Common pompano. Nos. 234, 263.

Pomatomus saltator ; Temnodon saltator, Günther. Blue fish ; Green fish ; Skip jack. No. 12.

Stromateus triacanthus. Butter fish ; Dollar fish ; Harvest fish ; La Fayette. No. 90.

Micropterus salmoides ; Huro nigricans, Günther. Large-mouthed black bass ; Black bass ; Oswego bass ; Green bass ; Bayou bass. No. 53.

Micropterus dolmieu ; Grystes fasciatus, Günther. Small-mouthed black bass. No. 91.

Perca fluviatilis ; (vid. Günther, Study of the Fishes, p. 375, and Jor. and Gil. p. 524) ; *Perca americana,* Jor. and Gil. Yellow perch ; American perch ; Ringed perch ; Perch. Nos. 127, 208.

Stizostedium vitreum ; Lucioperca americana, Günther. Pike perch ; Wall-eyed pike ; Dory ; Glass eye ; Yellow pike ; Blue pike ; Jack salmon. No. 52.

Stizostedium canadense, Jor. and Gil. ; *Lucioperca canadensis,* Günther, Pike perch ; Gray pike ; Sanger ; Sand pike ; Horn fish. No. 257.

Roccus lineatus ; Labrax lineatus, Günther. Striped bass ; Rock fish ; Rock. Nos. 7, 19, 225, 237, 248, 260.

Roccus americanus ; Labrax rufus, Günther. White perch. Nos. 44, 46.

Centropistris atrarius, Günther ; *Serranus atrarius,* Jor. and Gil. Sea bass ; Black fish ; Black sea bass. No. 251.

Epinephelus morio ; Serranus morio, Günther. Grouper; Red grouper. Nos. 114, 271.

Lutjanus blackfordi. Red snapper. Nos. 20, 26, 242.

Diplodus argyrops ; Pagrus argyrops, Günther. Porgy ; Porgee ; Scup ; Scuppaug. Nos. 15, 31, 262.

Diplodus probatocephalus ; Sargus ovis, Günther. Sheepshead ; Ger., Schafbrassen. Nos. 48, 250.

Sciæna ocellata. Red bass ; Channel bass ; Red horse. No. 270.

Menticirrus nebulosus ; Umbrina nebulosa, Günther. King fish ; Whiting ; Barb. No. 252.

Cynoscion regale ; Otolithus regalis, Günther. Weak fish ; Squeteague ; Gray trout. No. 273.

Tautoga onitis. Black fish ; Tautog ; Oyster fish. Nos. 38, 205, 244, 269.

Phycis chuss ; P. americanus, Günther. Hake ; Codling ; Squirrel hake. No. 113.

Brosmius brosne. Cusk. No. 110.

Gadus aeglefinus. Haddock ; Fr., L'anon ; Ger., Schellfisch. Nos. 16, 21, 229, 259.

Gadus morrhua. Common cod fish ; Fr., Morue ; Ger., Dorsch (young and fresh) ; Kabljau (old and fresh) ; Stockfisch (dried) ; Leberdan (salted). Nos. 5, 11, 25, 34, 37, 79, 80, 206, 228, 243.

Gadus tom-cod ; G. tomcodus, Günther. Tom cod ; Frost fish. No. 99.

Gadus virens. Pollock ; Pollack ; Coal fish ; Green cod ; Fr., Colin ; Ger., Köhler. No. 81.

Hippoglosus vulgaris ; Pleuronectes hippoglossus, Günther. Halibut ; Fr., Fletan ; Ger., Heilbutte. Nos. 1, 9, 211.

Platysomatichthys hippoglossoides ; Hippoglossus groenlandicus, Günther. Turbot ; Greenland halibut. No. 49.

Paralichthys dentatus ; Pseudorhombus dentatus, Günther. Common flounder. Nos. 2, 22,

Pleuronectes americanus. Winter flounder ; Mud dab. No. 253.

Petromyzon marinus. Lamprey eel ; Sea lamprey ; Fr., Lamproie ; Ger., Seeneunange. No. 236.

Raia sp. Skate. No. 247. (Only part of specimen received for analysis, not sufficient to identify species.)

II.—METHODS OF ANALYSIS.

The methods employed for preparing the materials for analysis, and for the analytical determinations, have been referred to in the reports of the U. S. Fish Commission[1] above mentioned, and are to be discussed in full in the detailed report. It will therefore suffice to speak of them very briefly here.

Separation of flesh from refuse. Sampling.—The sample as received at the laboratory was weighed, the flesh (edible portion)

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[1] See also Ber. d. deutsch. chem. Gesell. **16**, 1883, s. 1839.

separated from the refuse (bones, skin, entrails, spawn, etc.), and
both portions weighed. There was always a slight loss in cleaning,
due, evidently, to evaporation and to slimy and fatty matters and
small fragments of the tissues that adhered to the hands and to
the utensils used in preparing the sample. Perfect separation of
the flesh from the other tissues was difficult, but the loss resulting
from this was small, so that, though the figures obtained represent
somewhat less than was actually in the sample, yet the amount
thus wasted was doubtless scarcely more than would be left
unconsumed at an ordinary table. The reasons for rejecting the
skin, which generally has considerable nutritive value, were that
its chemical constitution is different from that of the flesh, and that,
so far as we have observed, it is not ordinarily eaten in this country.
With the closer domestic economy that increased density of popu-
lation must bring, people will doubtless become more careful here-
after to utilize such materials, and certainly a more accurate study
of their chemical constitution is to be desired.

In sampling the material for analysis, it was finely chopped and
well mixed in a wooden tray.

Water and water-free substance.— The drying was done in
ordinary water-baths of large size, at a temperature of nominally
100°, but actually about 96° (as is, I believe, usual in such drying
baths, which consist of an air chamber with double walls inclosing
boiling water). In each case, one or more samples of 50 to 100
grams each of the freshly chopped flesh were weighed on a watch
glass or small sauce plate, heated in a current of hydrogen for 24 to
48 hours, cooled, allowed to stand in the open air for some 24 hours,
weighed, ground, sifted through a sieve with circular holes of ·
1 mm. diameter, bottled, and set aside for analysis. A few of the
fattest samples, however, could not well be worked through so fine
a sieve ; for these, either a coarse sieve was used, or the substance
was crushed as finely as practicable and bottled without sifting.
For the complete drying, from 1 to 2 grams of the partly dried
material were weighed in small drying flasks, and dried in hydro-
gen three or four hours. It is extremely difficult to get an abso-
lutely constant weight, though we find that the object is in most
cases approximately attained in three hours. The total moisture
and water-free substance are computed from the two dryings.

The especial object in drying in hydrogen was to prevent possible
oxidation of fats, whereby the latter would be rendered insoluble

in ether, and the accuracy of their determination impaired. That this is at all necessary in animal tissues, or when it is necessary and when not, I am not prepared to affirm. But as a precaution in the early part of the work, we arranged an apparatus for drying in hydrogen,[1] and although the comparative trials in air and in hydrogen did not show any large differences in results, the apparatus was so convenient that we have used it throughout the investigation.

Drying in air.—As drying in air is nevertheless more convenient for large quantities, and suffices perfectly well for certain determinations, such as sulphur, phosphorus and chlorine, a sufficient quantity of material for this work was prepared by drying a portion in air. This was effected by weighing 200 grams or more of the freshly chopped substance at the same time that the portion was taken for drying in hydrogen, drying in the air-bath without hydrogen, exposing to air of room, weighing, grinding, and bottling as above.

Examination of the analytical details (in the detailed report) will show a number of cases in which the percentages of water-free substance in portions used for various determinations, nitrogen, fat, ash, etc., differ from those given in the water determination. This is due to the simple fact that some time intervened between the determinations, and that our experience showed that although reasonable care was used to procure bottles with well-fitting glass stoppers to hold the partly dried material, yet the moisture in the latter was liable to change on standing in the laboratory, and that both use of rubber stoppers and paraffine on the glass stoppers failed to prevent this so completely as to make us feel safe in using the substance after it had stood for more than a few days, without redetermination of the water.

Fats, Ether extract.—The fats were extracted with ether, which, after various trials with chloroform and benzine, we are persuaded is the most convenient solvent for the purpose.

The determinations were made in the material which had been nearly dried in hydrogen. Generally, from 0.3 to 1.0 gram was used for the extraction. The operation was conducted in an apparatus similar to that described by Johnson.[2] The corks and filter paper were always treated with ether before using. We have found it convenient, however, to duplicate the apparatus, using

[1] To be described elsewhere.   [2] Am. Jour. Sci. **13**, 1877, 190.

several at once. A rectangular box of zinc or galvanised iron, 70 or 80 cm. long, 17 cm. wide and 25 cm. high, and provided with six pipes of block tin which serve as worms, makes a very good cooler for the ether. We do not generally find it necessary to have a current of water running through the cooler, even in summer ; the radiation of heat from the water is sufficient to keep it cool enough to condense the ether without being changed.

The point at which the extraction is completed we have not always found easy to determine. The methods ordinarily recommended, of evaporating a drop of the ether after it percolated through the substance, either on a piece of paper or on a clean watch glass, and noting whether a transparent spot or a residue remains, have not in our experience been satisfactory. We prefer to continue the extraction for such time as experience has indicated to be sufficient, and then remove the flask and substitute another, repeating this latter operation until the new flask shows no gain in weight after the extraction has been continued for some time. When the extraction is believed to be complete, the apparatus is taken off from the condensing tube, the inner tube holding the substance is taken out, a test tube substituted, the apparatus put back in place, and the ether in the flask is again warmed, allowed to condense and run back into the test tube and thus most conveniently recovered for subsequent use. The small portion of ether still adhering to the extract in the flask is removed by warming in a current of hydrogen in the apparatus used for drying.

The flasks are always weighed against a similar flask as counterpoise.

What other substances besides fats are thus extracted from the flesh of fish, oysters, etc., is a matter which I have not investigated, contenting myself for the present with simply calling the material extracted by ether, ether extract. As the analytical details show, the material used for fat determination was nearly dried in the hydrogen before extraction with ether. By this means two possible sources of error are avoided, to wit :

1. Certain fatty substances, as is well known, are rendered insoluble or very difficultly soluble in ether by being heated in air. This alteration, due, I suppose, to oxidation, is very marked in many vegetable substances. Thus I have found the larger part of the fats of linseed, maize, and grasses to be rendered insoluble in this way. Whether or to what extent any of the fats of the animal

tissues which we have analysed would be thus affected is a matter which I regret to have been unable thus far to study. That the error by drying in air would be large seems to me improbable.

2. When the material extracted contains considerable quantities of water, or when commercial ether containing water is used, other substances than fats may possibly be dissolved. When and how greatly the presence of water would affect the results I cannot tell, though I do not believe the error would be great in such substances as we are here dealing with.

The ether extract was nearly always more or less colored. In how far this was due to chemical or physical changes in the fats, and in how far to coloring matters extracted with them, I cannot say.

As regards the difficulty of extracting with ether, our experience shows that many of the vegetable fats, as those of maize, wheat, etc., are easily extracted, while those of animal tissues are often more difficult to get into solution. The fat, or, more properly, the materials soluble in ether, are more readily extracted from oysters, clams, lean beef, etc., than from the flesh of the fatter fish and the fatter meats. In general, the greater the percentage of fat in a substance the more difficult do we find the removal of the last traces. Mr. Woods remarks that "the flesh of eels was the hardest material to extract I have ever met." I should say that even the flesh of eel could hardly be much more difficult than the yolk of eggs, which, however, is of different composition. It is, I think, very important that the material to be extracted be fine, especially when it is hard and dry, as is often the case with partly dried flesh.

After the experience which we have had in extracting with ether, I am persuaded that correct results are far harder to obtain than is ordinarily believed. Indeed, I regard these determinations as among the more difficult ones with which we have had to do.

Nitrogen, protein, albuminoids, etc.—The nitrogen was determined in the partly dried substance by soda-lime. Several series of experiments were undertaken to get light upon the conditions under which correct determinations of nitrogen in animal tissues may be made by this method. Part of them have been,[1] and the others, it is hoped, will be, described in this Journal. We have come to believe that with proper precautions, extremely accurate determinations may be made with soda-lime, but that great care is needed to insure them.

[1] Vol. **9**, page 311.

It is customary to compute the albuminoids or protein (nitrogenous substances) by multiplying the nitrogen by 6.25. In our analyses this factor has, in general, been very nearly correct. I have thought it best, for the present purpose, to state the percentages of nitrogen and of protein as calculated by multiplying these by 6.25, and also to estimate the " albuminoids, etc." by difference. For the latter, the remainder left after subtracting the sum of ether extract and ash from the water-free substance, or the sum of water, ether extract and ash from the fresh substance, is used. This is, of course, not absolutely correct, but it is more nearly so than the product of nitrogen by 6.25 would be. This subject, however, demands special discussion.

Ash.—The ash was determined by carbonising a portion of the partly dried material, in the case of flesh preferably about 5 grams, extracting the charred mass with water, burning the residue, adding the solution, evaporating and burning. The charring and burning were conducted in platinum capsules over a gas flame. The crude ash thus obtained was practically free from coal. No determinations of carbonic acid were made.

Phosphorus.—A portion of the partly dried substance, preferably about one gram, was carefully burned in a platinum crucible with some ten grams of a mixture of equal parts of sodium nitrate and carbonate, previously proved free from phosphoric acid. The white mass was dissolved in water, acidulated with nitric acid, evaporated, and treated with nitric acid again, the operation being repeated when necessary to remove chlorine, and the phosphoric acid then estimated with ammonium molybdate solution.

A number of experiments were made to test the accuracy of the determinations in the presence of such large quantities of sodium nitrate, etc., as are necessarily used. Awaiting their publication in detail, it will suffice here to give the outcome, which was briefly this :

At the temperature of the trials, which was in each case not far from 29° C., two precautions are necessary : (1) the use of a large excess of the molybdate solution (unless nitric acid alone should perform the same office), and (2) allowance of ample time for precipitation. Neglect of these precautions involves risk of loss of phosphoric acid. The effect of higher temperature was not tested. Practically, we have used 25 cc. of molybdate solution and allow from 36 to 48 hours for the precipitation.

Sulphur.—About one gram of the nearly dried substance was oxidised as for the determination of phosphorus. The cooled mass was dissolved in hydrochloric acid, and the sulphuric acid determined by precipitation with barium chloride.

. It is well known that the presence of salts of the alkalies, including sodium chloride, when present in considerable quantities, may affect the precipitation of sulphuric acid by barium chloride, the precipitate of barium sulphate bringing down with it under some circumstances more or less of the alkaline salt. The ordinary means for avoiding this consist in diluting the solution, precipitating hot, and washing the precipitate with hot water. In view of the large quantity of sodium chloride present in these determinations, it seemed desirable to study the conditions under which pure and impure barium sulphate precipitates are formed, a little more closely than had, so far as I am aware, been done. For this purpose a series of experiments were devised.

The plan consisted in taking a solution of sulphuric acid and determining the amount of acid both in the solution alone and after adding different quantities of sodium chloride. Comparative trials were made with concentrated and dilute solutions and by precipitating hot and cold. The sulphuric acid solution used was the same as employed for nitrogen determination with the soda lime. The sodium chloride solution contained about 25 per cent. of sodium chloride, and the barium chloride solution about 20 per cent. of the ordinary crystallised salt. Without going into details of the experiments, which will, I trust, be given later, it will suffice to say that, although when precipitated cold from concentrated solutions, the barium sulphate is apt to be too heavy, i. e. to bring down sodium chloride ; yet, when precipitated hot, or even precipitated cold from dilute solutions, it was uniformly pure. This is in accordance with the previous observations on which general practice is based. Our determinations served simply to show the limits of concentration and amount of sodium chloride within which it is safe to work. It should be noted, however, that the solutions contained in all cases a small, but only a small, amount of free hydrochloric acid, and that only a small excess of barium chloride was used in the precipitation. Practically, the ordinary way as recommended by Fresenius is accurate for these determinations, even in presence of large amounts of sodium chloride, provided the proper precautions are observed. The experiments

satisfied us that the presence of the sodium chloride in the determinations of sulphur, as we conducted them, did not interfere with the accuracy of the results.

Chlorine was determined by burning the partly dried substance in platinum evaporating dishes, as in the determinations of phosphorus and sulphur, and estimating the chlorine in the fused mass with ammonium sulphocyanide by Volhard's process.[1] Dr. Long, by whom the determinations were made, carried out, at my request, a series of experiments which led to the observance of certain precautions, and showed that with them very satisfactory results may be obtained in the determination of chlorine in such substances as those we were working with. The details of Dr. Long's experiments are reserved for publication with the experiments on phosphorus and sulphur above mentioned. The precautions are contained in the following statement of the method followed in the determinations of chlorine in fish flesh.

1. The substance was very slowly fused with a mixture of potassium nitrate and sodium carbonate so as to avoid any possible loss by spirting. It was observed that when the platinum capsule, in which the ignition was carried on, was covered with a watch glass, small portions of the substance were thrown out against it unless the operation was conducted very slowly. With care, however, there was no considerable loss, as indicated by either the appearance of the watch glass or actual determinations with sugar and a known amount of chlorine.

2. The fused mass was dissolved in chemically pure nitric acid, which was made quite dilute, since by using a stronger acid some chlorine could easily be driven off, as was found by experiment.

3. To the solution thus obtained an excess of silver nitrate solution (decinormal or half decinormal) was added, and the whole boiled on the water-bath for about two hours. This long boiling with excess of nitric acid, added after the silver nitrate, was found necessary to expel nitrous acid coming from the reduction of the nitrate in the fusion.

4. After the boiling, the solution was allowed to become quite cold before titrating.

Proximate ingredients directly determined.—In a number of the specimens, determinations were made of the ingredients soluble in cold and hot water, and of the portion not dissolved by water,

alcohol, or ether. The object was as much to test the methods commonly employed as to learn the amounts of the ingredients. The methods have proved unsatisfactory in many respects, and we have felt it advisable to make no more determinations by them than are indicated in the tables, until the subject is worked up more thoroughly. For that matter, an at all satisfactory examination of the proximate constituents will involve the study of a good deal more than the compounds of the flesh. Considering the complicated character of the compounds concerned, the vagueness of our present knowledge of them, and the amount of preliminary work that is always necessary before such an investigation can be got into good running order; and adding to all this the import-ance of studying the elementary composition of the organic com-pounds, the mineral ingredients as well, it is clear that much labor will be necessary to reach the desired results. Those we have obtained will at least serve to compare with similar ones obtained by other analysts.[1]

Cold-water extract.—Of the freshly chopped substance, 33⅓ grams were digested for eighteen to twenty-four, generally about twenty, hours in 500 cc. of cold water, and filtered. The filtration was conducted at first through "coffee filter paper," but we have found it better to use fine linen cloth, which has the advantages of more rapid filtration and of allowing the liquid to be squeezed through with proper care. The solids do not pass through the cloth more than through the filter paper, and by laying on a glass plate, scraping, and subsequent rinsing, they are separated much more easily and completely than they can be from the filter paper.

Albumen coagulated from cold-water extract.—The filtrate thus obtained was boiled and filtered through previously dried and weighed asbestos filters. After washing with ether, the filter with its contents was dried and weighed. That this method for deter-mining albumen is accurate is by no means proven or even probable. Indeed, in some species of fish at least—and the same is true of other animals—the cold-water extract of the muscular tissues contains a form of albumen, or at any rate a substance or substances closely resembling albumen, which is not precipitated by boiling at all, except after the addition of large quantities of acid or salts. When the determinations in question were made,

[1] See Almén, *Analyse des Fleisches einiger Fische,* Nova Acta Reg. Soc. Sc. Ups., Ser. III, Upsala, 1877.

this substance had not been well studied, but I was persuaded that the method followed was not reliable for the determination of the actual amount of albumen, a view which studies to be elsewhere discussed have amply confirmed.

Extractive matters. Cold-water extract not coagulated by boiling.—The filtrate from the coagulated albumen was evaporated in platinum capsules and weighed. One portion was used for determination of the ash, which was done by charring at a low temperature, extracting with water, igniting the residue until it was well burned, adding the water solution, evaporating, igniting carefully at a low temperature, and weighing. The other portion was finely ground, dried in air to determine the percentage of water, and extracted with ether until free from fat, usually two or three hours. The crude extract, minus the water, fat, and ash, is reckoned as pure extract, and is designated as "extractive matters." It of course contains the albumen which was not coagulated, the other nitrogenous compounds, the carbohydrates, and whatever else, except fats and mineral matters, was taken from the flesh of the fish by the digestion in cold distilled water.

Hot-water extract. "Gelatin."—The residue left after the extraction with cold water was treated for 18 to 24 hours, generally about 20 hours, with distilled water at 100° or slightly below. It was then filtered through weighed asbestos filters, and the filtrate evaporated to dryness in platinum, and weighed as "crude gelatin." In this fat and ash were determined, and the pure extract, called in the tables "gelatin," estimated as in the cold-water extract. It should be stated that in both hot and cold water extracts, the figures for total extract in the tables represent water-free substance, i. e. crude extract minus water. I am inclined to think it would be better to determine both water and fat in the crude extracts in one operation by extracting with ether and noting the loss.

Insoluble protein.—The residue left after the extraction with hot water was treated with alcohol or ether, or both, dried and weighed. Water, ash, and fat were then determined (except, of course, that fat was not determined in the cases where it had been previously extracted). The ash was determined by direct burning, it being assumed that the previous treatment with cold and hot water had sufficed to remove the easily fusible and volatile salts. The removal of the last portions of fat is often extremely difficult,

and it is not impossible that in some cases traces were left and weighed as insoluble protein. The figures for total insoluble protein in the tables denote water-free substance.

It is perhaps superfluous to state that the determinations were all made in duplicate. The figures given in the tables which follow represent the averages of the closely agreeing results. The analytical details are to be given in full in the monograph mentioned above.

III.—TABULAR STATEMENTS OF ANALYSES.

Tables I to X recapitulate the results of the analyses of American fishes.

Table I gives the localities of the specimens as stated by the parties from whom they were received, the portions received for analysis, results of weighings in preparing for analysis, etc. The "loss in preparing for analysis" I suppose to have consisted chiefly of water which evaporated during the process, and of material which adhered to the hands and the instruments with which the separations were made. The specimens are here put, for convenience, in numerical order. The full report referred to will contain further descriptions and details regarding these specimens, and will give similar data for preserved fish, which are omitted from the present condensed account.

Table II gives results of analyses of flesh calculated on water-free substance. It will be observed that the percentages of protein as estimated by multiplying the nitrogen by the factor 6.25, and those of "albuminoids, etc." (actual nitrogenous substances) as estimated by difference [100—(ether extract + ash) = albuminoids, etc.], are both given. The former (protein = N × 6.25) has the sanction of common usage, but the latter comes nearer to the truth. We certainly cannot go far away in assuming that the flesh of fish contains ordinarily but very little of non-nitrogenous compounds other than fats and mineral compounds, though a more thorough study of the carbohydrates and complex nitrogenous and phosphorised fats is much needed. Accordingly it seems to me that in these analyses the most accurate measure of the nitrogenous compounds is to be found by subtracting the sum of the ether extract and ash from the whole.

Table III gives analyses of flesh calculated on fresh substance, and includes both protein as estimated by multiplying N by 6.25,

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and "albuminoids, etc.," by difference [100 — (water + ether extract + ash) = albuminoids, etc.] The figures of this table are computed from those of Table II, the percentages of water and water-free substance in the flesh and of ingredients in water-free substance serving as the basis of the calculations. In the subsequent tables, deduced from these and taken as representing the actual composition of the flesh, the latter figures rather than those obtained by multiplying N by 6.25 are taken as representing the nitrogenous matters.

It will be interesting to observe the differences between results obtained by estimating the nitrogenous substance in this way (see section on "Nitrogen, Protein, etc." in chapter on Methods of Analysis, above) and by multiplying the percentage of nitrogen by the factor 6.25. The figures of Table IV give the sum of protein ($N \times 6.25$), ether extract, and ash in the water-free substance, and of these and water in the flesh, both of the specimens in Tables II and III and of those of "prepared fish" in Tables VIII and IX beyond. If we leave the carbohydrates out of account, assume the ash to represent the mineral matters, and take ether extract as representing the fats, but as including no nitrogenised fats, then the figures for "albuminoids, etc., by difference" will represent exactly the amount of nitrogenous substance (albuminoids, gelatinoids, nitrogenous extractives, and nitrogenised fats). Of course, these assumptions are not absolutely correct. The flesh contains a minute quantity of carbohydrates (including all non-nitrogenous substances other than fats) ; the ash is not the exact measure of the mineral matters, and the ether extract does not exactly represent the neutral fats. But the errors involved are small, and until better methods of analysis are devised and brought into current use, "albuminoids, etc., by difference" will be the closest approach to the actual nitrogenous substance.

The current method of estimating the nitrogenous material is by multiplying the nitrogen by 6.25. To this product, various terms, as albuminoids, proteids and protein, are applied. If the figures for "albuminoids, etc., by difference" were the exact measure of the nitrogenous substance, the difference between them and the product of $N \times 6.25$ would be the error in computing protein in this latter way. In Table II, the ash + ether extract + "albuminoids by difference" = 100, and the ash + ether extract + protein ($N \times 6.25$) =

a quantity varying more or less from 100. On the assumption that the " albuminoids by difference" represent the actual nitrogenous substance, the variations from 100 in the latter figures represent the error in calculating protein by multiplying N by 6.25.

Of course, the correct determination of actual nitrogenous substance involves numerous other questions in addition to those here suggested, and first of all, the chemical and physiological distinctions between the different nitrogenous compounds. But for the present purpose it will suffice to take the "albuminoids, etc., by difference" as the measure of the nitrogenous material.

Table IV gives the sum of ash $+$ fat $+$ protein ($N \times 6.25$) in water-free substance, and of water $+$ ash $+$ fat $+$ protein ($N \times 6.25$) in flesh, of the specimens of fish in Tables II and III, and of prepared fish in Tables VIII and IX beyond. For the water-free substance the range of the figures is from 97.01 to 116.01, but in the flesh (leaving the preserved fish out of account) the range is only from 99.34 to 102.85, or, omitting the skate, to 101.14. The only cases in which the sum is below 99 in the water-free substance of the fresh flesh are those of the spent salmon. In these, both nitrogenous substance and fat had been reduced during the spawning season. The only ones above 101 in the flesh are two specimens of fat salmon, one each of sea bass and turbot, several of cod, and one of skate. It is clear that the use of either the figures for protein, $N \times 6.25$, or "albuminoids, etc., by difference" for the total nitrogenous substance in the flesh, will involve no very serious error except in the last named cases.

The figures for protein in sea bass, turbot, cod, and especially skate, are a little surprising. The question naturally suggests itself whether there may not be errors in the analyses. I think the analytical details, when published, will show that this explanation is extremely improbable. All the nitrogen determinations in the specimens of cod gave large figures. Two determinations in the specimens of skate gave respectively 16.28 and 16.29 per cent. in the water-free substance. These figures are so large that a third determination was made, with 16.30 as the result.

In brief, while the error involved in estimating the total nitrogenous substance by multiplying the nitrogen by the factor 6.25 in the usual way, is, when viewed from the exact scientific standpoint, very considerable in many cases, it is seldom large enough to be of great practical importance. The exceptional cases, however, demand further study.

TABLE I.

List of Specimens of American Fishes Analyzed, Names, Localities, and Proportions of Flesh, etc.

Kinds of Fish, Localities, and Portion Taken for Analysis.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Total Weight of Specimen (lbs.)	(oz.)	(grams)	Proportion of Flesh, etc., in Specimen as taken for Analysis — Flesh, Edible Portion. (per ct.)	Refuse, Bones, Skin, Entrails, etc. (per ct.)	Loss in Preparation for Analysis. (per ct.)
Halibut, posterior part of body, lean	1	Spring	...	4	2.7	1894.0	75.92	23.12	0.96
Common flounder, entrails removed	2	"	2	5	1.2	2308.0	41.33	57.02	1.65
Cod, head and entrails removed	3	"	2	6	1.9	2780.0	69.57	28.70	1.73
Eel (salt water), skin, head and entrails removed	4	"	11	3	0.1	1368.0	76.24	21.42	2.34
Alewife, whole, Connecticut River	5	"	12	1	14.2	859.0	49.48	50.52	...
Shad, whole, Hudson River, first of season	6	"	2	4	3.8	1925.0	48.31	49.35	2.34
Striped bass, whole, Connecticut River	7	"	1	4	8.4	2055.0	42.09	56.69	1.22
Mackerel, whole	8	"	4	2	13.0	1280.0	60.55	38.28	1.17
Halibut, section of body, fatter than No. 1	9	"		2	6.0	1075.0	88.28	11.16	0.56
Shad, whole, Connecticut River, early in season	10	"	1	3	8.2	1595.0	52.35	46.40	1.25
Cod, head and entrails removed	11	"	1	5	9.2	2532.0	68.13	30.57	1.30
Blue fish, entrails removed	12	"	1	3	1.3	1400.0	50.14	48.57	1.29
Mackerel, whole	13	"	2	–	15.7	898.2	45.76	51.77	2.47
Salmon, entrails removed, Maine	14	"	1	10	8.0	4764.3	76.16	23.84	...
Porgy, whole	15	"	4	2	9.9	1190.5	33.16	65.17	1.67
Haddock, entrails removed	16	"	1	4	2.9	1900.0	46.84	51.42	1.74
Lake trout (Mackinaw trout), whole, Lake Ontario	17	November	1	7	14.8	3600.4	43.31	56.32	0.37
White fish, whole, Lake Champlain	18	"	1	2	14.3	1313.0	45.76	53.47	0.77
Striped bass, whole, Bridgeham, Long Island	19	"	1	2	6.7	1098.5	42.51	56.90	0.59
Red snapper, whole, Fernandina, Florida	20	"	7	7	11.7	3597.5	60.00	39.60	0.40
Haddock, entrails removed, Rockaway, Long Island	21	"	5	5	4.7	2402.0	47.50	51.62	0.88
Common flounder, whole, Amagansett, Long Island	22	March	2	2	12.3	1257.5	31.97	66.80	1.23
Smelt, whole, Hackensack River, New Jersey	23	"	73	2	4.0	1023.0	61.78	34.82	3.40
Brook trout, whole, cultivated, Long Island	24	"	6	2	13.6	1295.0	46.95	50.11	2.94
Red snapper, entrails removed, Florida, East coast	26	April	1	12	1.6	5498.7	47.36	52.45	0.19

TABLE I.—*Continued.*

Kinds of Fish, Localities, and Portion Taken for Analysis.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Total Weight of Specimen.		Proportion of Flesh, etc., in Specimen as taken for Analysis.			
				lbs.	oz.	grams. Flesh, Edible Portion.	per ct. Flesh, Edible Portion.	per ct. Refuse, Bones, Skin, Entrails, etc.	per ct. Loss in Preparation for Analysis.
Mackerel, whole, Cape May, New Jersey	30	May,	4	5	11.3	2594.0	50.29	48.85	0.86
Porgy, whole, Rhode Island	31	"	4	6	4.6	2857.0	41.65	57.33	1.02
Shad, whole, Connecticut River	32	"	1	3	13.7	1752.0	52.80	45.89	1.31
Black fish, whole, Stonington, Connecticut	38	December.	2	4	8.6	2060.0	42.16	56.15	1.69
Mackerel, whole, Cape Cod, Massachusetts	39	"	1	1	2.4	522.1	64.60	33.78	1.62
Spanish mackerel, whole	43	March.	1	3	5.2	1512.4	64.02	34.61	1.37
White perch, whole	44	"	1	1	11.1	770.1	35.24	63.24	1.52
Mascalonge, whole, St. Lawrence River	45	"	2	9	1.0	4118.0	50.57	49.23	0.20
White perch, whole	46	"	4	2	0.9	935.9	36.24	61.80	1.96
Herring, whole	47	"	4	2	6.0	1080.8	51.13	46.00	2.87
Sheepshead, entrails removed, Florida	48	"	1	5	5.5	1974.2	42.07	56.59	1.34
Turbot, or Greenland halibut, whole, Newfoundland	49	"	1	5	8.0	2496.5	52.27	46.04	1.69
Pike perch, or Wall-eyed pike, whole	52	"	2	3	7.5	1122.7	41.21	57.25	1.54
Large-mouthed black bass, whole, North Carolina	53	"	1	3	11.1	1676.5	43.16	56.05	0.79
Salmon (female), whole, Penobscot River	77	July,	1	13	1.8	5948.0	66.54	32.98	0.48
Salmon (female), whole, Penobscot River	78	"	1	11	3.3	5082.0	69.22	30.58	0.22
Pollock, head and entrails removed, Massachusetts coast	81	October,	1	5	13.1	2638.0	66.64	28.50	1.86
Butter fish, whole, east end of Long Island	90	November.	4	1	9.6	724.0	55.86	42.76	1.38
Small-mouthed black bass, whole, Seneca Lake, N. Y.	91	"	2	1	11.2	772.8	45.36	53.66	0.98
Pike, entrails removed, Lake Ontario	98	"	1	3	9.0	1617.0	55.69	42.67	1.64
Tom-cod, whole, south side of Long Island	99	"	4	2	7.6	1131.6	39.06	59.88	1.06
Pickerel, whole, Seneca Lake, New York	100	"	3	2	2.5	960.6	53.14	45.44	1.42
Cusk, entrails removed, Massachusetts coast	110	December.	1	3	2.7	1436.5	58.40	40.28	1.32
Cisco, whole, Lake Erie	111	"	4	2	12.4	1256.0	55.95	42.70	1.35
Hake, entrails removed, off Coney Island, New York	113	"	1	14	6.5	6534.5	47.54	52.46	...
Grouper (Red grouper), entrails removed, Pensacola, Florida	114	"	1	3	7.0	1559.0	43.55	55.77	0.68
Mullet, whole, Virginia	126	"	1	1	8.9	707.5	40.99	57.88	1.13
Yellow perch, whole, Lake Champlain	127	"	4	2	8.8	1152.0	36.56	62.64	0.80

TABLE I.—Continued.

Kinds of Fish, Localities, and Portion Taken for Analyses.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Total Weight of Specimen. (lbs.)	Total Weight (oz.)	Total Weight (grams.)	Flesh, Edible Portion. (per ct.)	Flesh, Bones, Skin, Entrails, etc. (per ct.)	Loss in Preparation for Analysis. (per ct.)
Black fish, whole.	205	March.	—	3	3.0	1446.5	33.95	64.08	1.97
Cod (Rock cod), whole, near Block Island.	206	"	—	4	2.3	1881.0	42.85	56.51	0.64
Smelt, whole, Maine coast.	207	"	14	0	14.0	398.0	47.99	48.99	3.02
Yellow perch, head, entrails, fins and tail removed, Connecticut River.	208	"	6	0	10.7	302.0	60.60	35.10	4.30
Halibut, sections of different parts of body, George's Banks.	211	"	—	8	2.7	3705.0	79.52	18.70	1.78
Shad, whole, Delaware River.	212	April.	—	2	10.2	1196.0	53.77	44.39	1.84
Eel (salt water), head, skin and entrails removed, north coast Long Island.	217	"	6	0	15.4	436.0	76.14	19.04	4.82
Alewife, whole, Connecticut River.	220	"	1		14.8	879.2	47.09	49.42	2.68
Shad, whole, Connecticut River.	221	"	—	3	3.5	1461.0	45.18	53.25	1.57
Pickerel, whole, Connecticut River.	224	"	2		5.2	600.0	48.16	48.67	3.17
Striped bass, whole, Long Island Sound.	225	"	2		7.9	1132.0	49.63	48.59	1.78
Cod, head and entrails removed.	228	"		7	7.4	3387.0	72.92	25.54	1.56
Haddock, entrails removed.	229	"		4	4.2	1480.0	49.73	47.97	2.30
Mackerel, entrails removed.	230	"	2		6.6	640.0	57.35	40.65	2.00
California salmon, section of anterior part of body.	233	"		14.7		870.5	88.70	10.34	0.96
Pompano, whole, Pensacola, Florida.	234	"		1	8.1	683.5	56.24	42.37	1.39
Lamprey eel, whole, Hackensack River.	236	"	2		13.6	1295.0	50.49	45.79	3.81
Striped bass, whole, North Carolina.	237	"	2		12.8	1270.0	41.37	57.08	1.55
Sturgeon, section of anterior part of body, Delaware River.	238	"		1	10.6	753.0	84.72	14.41	0.87
Red snapper, entrails and gills removed, Pensacola, Florida.	242	"		1	1.2	848.0	54.33	45.29	0.38
Cod, whole, Long Island.	243	"		5	7.5	2481.0	49.78	48.53	1.69
Black fish, entrails removed, Massachusetts.	244	"	2		8.5	1147.0	40.80	57.81	1.39
Shad, whole, Hudson River.	245	"		3	7.7	1579.0	45.92	52.69	1.39
Skate, left lobe of body.	247	"		4	11.9	2150.0	46.32	51.03	2.65
Striped bass, whole, Long Island.	248	"	2		0.0	906.0	42.93	55.41	1.66
Shad, whole, North Carolina.	249	"		3	15.6	1801.0	39.75	58.75	1.50
Sheepshead, whole, North Carolina.	250	"		1	15.3	886.5	32.61	65.98	1.41
Sea bass, whole, Pensacola, Florida.	251	"		6	9.3	2985.0	43.84	56.09	0.07

TABLE 1.—Concluded.

Kind of Fish, Localities, and Portion Taken for Analysis.	Laboratory Numbers of Specimens.	Specimen Received.	Number of Fish in Specimen.	Total Weight of Specimen. lbs.	oz.	grams.	Proportion of Flesh, etc., in Specimen as Taken for Analysis. Flesh, Edible Portion. per ct.	Refuse.—Bones, Skin, Entrails, etc. per ct.	Loss in Preparation for Analysis. per ct.
King fish, whole, North Carolina...................................	252	April.	1	1	8.2	685.5	42.16	56.60	1.24
Winter flounder, whole, Rhode Island coast..................	253	"	1	1	10.5	751.0	41.16	56.20	2.64
Brook trout, whole, cultivated, Long Island...................	254	"	3	0	12.3	353.1	51.15	45.20	3.65
Lake trout (Mackinaw trout), entrails removed, Lake Ontario......	255	"	1	5	7.4	2477.0	63.58	35.21	1.21
Brook trout, whole, Montreal, Canada...........................	256	"	1	0	12.2	346.0	48.86	49.12	2.02
Pike perch, or Gray pike, whole, Cleveland, Ohio	257	"	1	0	12.3	349.5	35.20	63.23	1.57
Small-mouthed red horse, entrails removed, Cleveland, Ohio	258	"	1	3	5.0	1500.0	46.20	52.47	1.33
Coast haddock, entrails removed, Long Island...............	259	"	1	7	2.1	3235.0	46.09	52.89	1.02
Striped bass, entrails removed, Long Island coast.........	260	"	1	2	2.2	969.5	47.96	51.16	0.88
Mackerel, whole, Virginia Capes...................................	261	"	1	1	4.4	576.0	48.43	50.35	1.22
Porgy, whole, Gravesend Bay, Long Island....................	262	"	1	1	5.6	896.0	41.70	57.58	0.72
Pompano, whole, Pensacola, Florida.............................	263	May.	1	2	1.5	949.0	50.39	48.56	1.05
Black fish, entrails removed, Rhode Island	269	"	1	2	0.0	1189.0	45.30	53.57	1.13
Red bass, whole, North Carolina...................................	270	"	1	6	11.1	3933.0	45.39	53.53	...
Red grouper, entrails removed, Pensacola, Florida	271	"	1	11	12.5	5344.0	44.05	55.95	...
Weak fish, whole, Long Island.....................................	273	"	2	2	0.0	909.4	47.01	51.89	1.10
Salmon (female), whole, Penobscot River, Maine..........	279	June.	1	11	3.5	5107.0	64.27	35.73	...
Salmon (male), whole, Penobscot River, Maine.............	280	"	1	12	10.0	5826.0	60.45	39.55	...
ROE.									
Shad roe, from shad No. 245......................................	246	April.	...	0	9.0	257.0	100.00	...	...
SPENT FISH.									
Salmon (male), whole, Penobscot River, Maine.............	35	November.	2	18	11.3	8482.7	55.72	43.78	0.50
Salmon (female), whole, Penobscot River, Maine..........	36	"	2	22	8.0	10204.9	56.18	43.54	0.27
Land-locked salmon (male), whole, Grand Lake Stream, Maine	40	December.	4	12	8.6	5686.3	50.74	48.41	0.85
Land-locked salmon (female), whole, Grand Lake Stream, Maine	41	"	4	7	15.8	3622.3	52.50	46.20	1.30

TABLE II.

Composition of Water-free Substance of Flesh of American Fishes.

Names of Fish.	Laboratory Number of specimens.	Nitrogen.	Protein, N × 6.25.	Fats. Ether Extract.	Ash.	Protein + Fats + Ash.	Albuminoids, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Sturgeon	238	13.63	85.19	8.90	6.72	100.81	84.38
Small-mouthed red horse	258	13.43	83.94	10.98	5.56	100.48	83.16
Herring	47	9.87	61.69	35.55	4.83	102.07	59.62
Alewife	5	12.61	78.81	15.88	6.08	100.77	78.04
"	220	11.67	72.94	22.28	5.48	100.70	72.24
" Average of 2 specimens		12.14	75.87	19.08	5.78	100.73	75.14
Shad	6	9.83	61.44	35.67	4.26	101.37	60.07
"	10	9.19	57.38	39.10	4.26	100.74	56.64
"	32	9.90	61.88	34.50	4.58	100.96	60.92
"	212	10.06	62.87	35.32	3.09	101.28	61.69
"	221	11.48	71.75	23.24	5.46	100.45	71.30
"	245	10.57	66.06	29.10	5.52	100.68	65.38
"	249	11.06	69.13	26.58	5.16	100.87	68.26
" Average of 7 specimens		10.30	64.36	31.93	4.62	100.91	63.47
Smelt	23	13.32	83.25	9.76	10.08	103.09	80.16
"	207	13.66	85.38	7.55	6.24	99.17	86.21
" Average of 2 specimens		13.49	84.31	8.65	8.16	101.13	83.19
White fish	18	12.16	76.00	21.51	5.36	102.87	73.13
Cisco	111	12.92	80.75	14.59	5.25	100.59	80.16
California salmon	27			51.59	2.98		45.43
"	233	8.37	52.31	46.51	2.85	101.67	50.64
" Average of 2 specimens				49.05	2.92		48.03
Salmon	14	9.57	59.81	37.94	3.35	101.10	58.71
" Female	77	9.47	59.19	40.98	4.26	104.43	54.76
"	78	9.71	60.69	38.20	4.19	103.08	57.61
" Male	279	10.24	64.00	33.76	3.51	101.27	62.73
"	280	10.17	63.56	33.53	3.73	100.82	62.74
" Average of 5 specimens		9.83	61.45	36.88	3.81	102.14	59.31
Spent salmon. Male	35	12.39	77.44	17.66	4.51	99.61	77.83
" Female	36	12.93	80.81	12.98	5.36	99.15	81.66
" Average of 2 specimens		12.66	79.13	15.32	4.93	99.38	79.75

Table II.—Continued.

Names of Fish.	Laboratory Numbers of Specimens.	Nitrogen.	Protein, N × 6.25.	Fats, Ether Extract.	Ash.	Protein + Fats + Ash.	Albuminoids, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Spent land-locked salmon. Male	40	11.70	73.13	18.12	5.76	97.01	76.12
" " Female	41	13.26	82.88	9.36	5.76	98.00	84.88
" " Average of 2 specimens	...	12.48	78.00	13.74	5.76	97.50	80.50
Lake trout	17	9.04	56.50	40.14	4.33	100.97	55.53
"	255	10.19	63.69	33.47	3.85	101.01	62.68
" Average of 2 specimens	...	9.62	60.10	36.80	4.09	100.99	59.11
Brook trout	24	13.25	82.81	11.61	6.33	100.75	82.06
"	254	14.92	93.25	3.72	4.75	101.72	91.53
"	256	13.41	83.81	12.14	5.08	101.03	82.78
" Average of 3 specimens	...	13.86	86.62	9.16	5.39	101.17	85.46
Pickerel	100	14.63	91.43	2.58	6.14	100.15	91.28
"	224	14.86	92.88	2.38	5.46	100.72	92.16
" Average of 2 specimens	...	14.74	92.15	2.48	5.80	100.43	91.72
Pike	98	14.78	92.38	2.87	5.07	100.32	92.06
Mascalonge	45	13.58	84.87	10.70	6.63	102.20	82.67
Eel, salt water	4	10.20	63.75	34.23	3.04	101.02	62.73
"	217	10.68	66.75	29.62	3.60	100.53	66.22
" Average of 2 specimens	...	10.44	65.25	31.92	3.66	100.77	64.48
Mullet	126	12.40	77.50	18.45	4.66	100.61	76.89
Mackerel	8	13.72	85.75	10.31	4.67	100.73	85.02
"	13	10.89	68.06	27.26	4.83	100.15	67.91
"	30	11.25	70.31	27.04	5.02	102.37	67.94
"	39	8.48	53.00	45.28	4.11	102.39	50.61
"	230	11.85	74.06	22.28	4.60	100.94	73.12
"	261	12.66	79.10	17.13	5.23	101.46	77.64
" Average of 6 specimens	...	11.47	71.71	24.88	4.75	101.34	70.8
Spanish mackerel	43	10.76	67.25	29.56	4.71	101.52	65.73
Pompano	234	9.00	56.25	41.40	2.95	100.60	55.65
"	263	14.16	88.50	7.51	4.69	100.70	87.80
" Average of 2 specimens	...	11.58	72.37	24.46	3.82	100.65	71.72
Blue fish	12	14.42	90.13	5.79	5.91	101.83	88.30
Butter fish	90	9.60	60.00	36.80	3.82	100.62	59.38
Large-mouthed black bass	53	14.54	90.88	4.47	5.57	100.92	89.96

TABLE II.—*Continued.*

Names of Fish	Laboratory Numbers of Specimens	Nitrogen.	Protein, N × 6.25.	Ether Extract. Fats.	Ash.	Protein + Fats + Ash.	Albuminoids, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Small-mouthed black bass............	91	13.79	86.19	9.69	4.93	100.81	85.38
Yellow perch.....	127	14.54	90.88	2.81	5.86	99.55	91.33
"	208	14.37	89.81	5.11	6.12	101.04	88.77
" " Average of 2 specimens..........	...	14.46	90.34	3.96	5.99	100.29	90.05
Pike perch, Wall-eyed pike	52	14.67	91.69	2.31	6.75	100.75	90.94
Pike perch, Gray pike	257	14.94	93.38	3.95	5.00	103.23	90.15
Striped bass..........	7	14.25	89.05	7.47	5.51	102.03	87.02
"	19	13.40	83.78	10.49	5.69	100.96	82.82
"	225	13.36	83.50	12.35	4.92	100.77	82.73
"	237	12.90	80.63	15.02	5.23	100.88	79.75
"	248	13.72	85.75	9.93	5.05	100.73	85.02
"	260	12.32	77.00	19.75	3.92	100.67	76.33
" " Average of 6 specimens..........	...	13.32	83.28	12.50	5.22	101.00	82.28
White perch..........	44	11.79	73.69	23.07	4.56	101.32	72.37
"	46	13.59	84.94	10.42	5.27	100.63	84.31
" " Average of 2 specimens	...	12.69	79.31	16.74	4.92	100.97	78.34
Sea bass	251	15.34	95.88	2.36	6.80	105.04	90.84
Grouper	114	14.88	93.00	2.39	5.79	101.18	91.82
"	271	15.06	94.13	3.39	5.42	102.94	91.19
" " Average of 2 specimens............	...	14.97	93.57	2.89	5.66	102.06	91.51
Red snapper..........	20	14.82	92.63	2.85	5.82	101.30	91.33
" "	26	13.96	87.25	8.58	5.86	101.69	85.56
" "	242	15.26	95.38	2.67	6.48	104.53	90.85
" " Average of 3 specimens............	...	14.68	91.75	4.70	6.05	102.50	89.25
Porgy..........	15	13.74	85.88	7.18	6.88	99.94	85.94
"	31	10.77	67.31	28.04	4.81	100.16	67.15
"	262	11.65	72.81	22.54	5.22	100.57	72.24
" " Average of 3 specimens.........	...	12.05	75.33	19.25	5.64	100.22	75.11
Sheepshead..........	48	11.90	74.38	24.02	3.93	102.33	72.05
"	250	14.81	92.56	3.16	6.36	102.08	90.48
" **Average of 2 specimens**.........	...	13.36	83.47	13.59	5.14	102.20	81.27
Red bass..........	270	14.65	91.56	2.89	6.67	101.12	90.44
King fish........	252	14.57	91.08	4.53	5.68	101.29	89.79

Table II.—*Concluded.*

Names of Fish.	Laboratory Numbers of Specimens.	Nitrogen.	Protein, N × 6.25.	Fats. Ether Extract.	Ash.	Protein + Fats + Ash.	Albuminoids, etc. (by difference.)
		per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Weak fish	273	13.54	84.63	11.37	5.64	101.64	82.99
Black fish	38	13.42	83.88	12.20	5.54	101.62	82.26
"	205	15.12	94.52	2.95	3.48	100.95	93.57
"	244	14.86	92.88	3.05	5.05	100.98	91.90
"	269	14.07	87.94	6.69	6.30	100.93	87.01
" Average of 4 specimens		14.37	89.81	6.22	5.09	101.12	88.69
Hake	113	14.56	91.00	3.97	5.77	100.74	90.26
Cusk	110	15.10	94.38	0.94	4.98	100.30	94.08
Haddock	16	15.08	94.25	0.85	5.82	100.92	93.33
"	21	14.77	92.31	0.78	8.72	101.81	90.50
"	229	14.97	93.56	1.82	6.78	102.16	91.40
"	259	15.27	95.44	1.93	5.71	103.08	92.36
" Average of 4 specimens		15.02	93.89	1.34	6.76	101.99	91.90
Cod	3	15.00	93.75	1.66	7.62	103.03	90.72
"	11	15.50	96.88	2.39	7.60	106.87	90.01
"	206	15.20	95.00	1.54	7.22	103.76	91.24
"	228	15.30	95.63	1.89	6.03	103.55	92.08
"	243	15.10	94.38	2.89	6.95	104.22	90.16
" Average of 5 specimens		15.22	95.13	2.07	7.08	104.28	90.84
Tom-cod		14.95	93.44	2.08	5.32	100.84	92.60
Pollock	99	14.41	90.06	3.23	6.45	99.74	90.32
Halibut	81	13.46	84.06	10.59	5.53	100.18	83.88
"	1	9.93	62.06	35.41	3.83	101.30	60.76
"	9	13.67	85.43	11.95	3.81	101.19	84.24
" Average of 3 specimens	211	12.35	77.18	19.32	4.39	100.89	76.29
Turbot	49	8.25	51.56	50.36	4.47	106.39	45.17
Common flounder	2	14.35	89.69	3.73	7.67	101.09	88.60
"	22	14.14	88.38	5.18	8.63	102.19	86.19
" Average of 2 specimens		14.24	89.03	4.46	8.15	101.64	87.39
Winter flounder	253	14.86	92.88	2.85	7.68	103.41	89.47
Lamprey eel	236	8.30	51.88	46.03	2.27	100.18	51.70
Skate	247	16.29	101.82	7.81	6.38	116.01	85.81

TABLE III.

Composition of Flesh of American Fishes.

Kind of Fish	Laboratory Numbers of Specimens	Water. per cent.	Water-free Substance. per cent.	Albuminoids, etc. (by difference). per cent.	Fats, Ether Extract. per cent.	Ash. per cent.	Nitrogen. per cent.	Protein, N × 6.25. per cent.	Water + Protein + Fats + Ash. per cent.
Sturgeon	238	78.71	21.29	17.96	1.90	1.43	2.90	18.11	100.15
Small-mouthed red horse	258	78.56	21.44	17.90	2.35	1.19	2.88	17.99	100.09
Herring	47	69.03	30.97	18.46	11.01	1.50	3.06	19.12	100.66
Alewife	5	75.92	24.08	18.80	3.82	1.46	3.04	19.00	100.20
....	220	72.96	27.04	19.54	6.02	1.48	3.16	19.72	100.18
" Average of 2 specimens		74.44	25.56	19.17	4.92	1.47	3.10	19.36	100.19
Shad	6	69.65	30.35	18.25	10.80	1.30	2.98	18.64	100.39
....	10	65.34	34.66	19.68	13.50	1.48	3.18	19.89	100.21
....	32	70.75	29.25	17.83	10.08	1.34	2.89	18.08	100.25
....	212	71.04	28.96	17.83	10.23	0.90	2.91	18.19	100.36
....	221	71.98	28.02	19.98	6.51	1.53	3.22	20.10	100.12
....	245	72.14	27.86	18.24	8.08	1.54	2.94	18.40	100.16
....	249	73.56	26.44	18.05	7.03	1.36	2.92	18.27	100.22
" Average of 7 specimens		70.62	29.38	18.56	9.47	1.35	3.01	18.83	100.27
Smelt	23	80.16	19.84	15.90	1.94	2.00	2.64	16.52	100.62
....	207	78.16	21.84	18.83	1.65	1.36	2.98	18.65	99.83
" Average of 2 specimens		79.16	20.84	17.37	1.79	1.68	2.81	17.59	100.22
White fish	18	69.83	30.17	22.06	6.49	1.62	3.67	22.93	100.87
Cisco	111	76.15	23.85	19.12	3.48	1.25	3.08	19.26	100.14
California salmon	27	62.68	37.32	16.96	19.25	1.11			
....	233	64.53	35.47	17.96	16.50	1.01			
" Average of 2 specimens		63.61	36.39	17.46	17.87	1.06	2.89	18.06	100.60
Salmon	14	67.15	32.85	19.17	12.47	1.21	3.14	19.63	100.46
" Female	77	63.41	36.59	20.04	14.99	1.56	3.47	21.66	101.62
....	78	65.08	34.92	20.12	13.34	1.46	3.39	21.19	101.07
....	279	61.37	38.63	24.23	13.04	1.36	3.96	24.72	100.49
" Male	280	61.03	38.97	24.45	13.07	1.45	3.96	24.77	100.32
" Average of 5 specimens		63.61	36.39	21.60	13.38	1.41	3.58	22.39	100.79
Spent salmon. Male	35	75.27	24.73	19.24	4.37	1.12	3.06	19.15	99.91
" Female	36	78.20	21.80	17.80	2.83	1.17	2.82	17.62	99.82
" Average of 2 specimens		76.74	23.26	18.52	3.60	1.14	2.94	18.39	99.87

TABLE III.—*Continued.*

Kind of Fish.	Laboratory Numbers of Specimens.	Water.	Water-free Substance.	Albuminoids, etc. (by difference).	Ether Extract. Fats.	Ash.	Nitrogen.	Protein, N × 6.25.	Water + Protein + Fats + Ash.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Spent land-locked salmon. Male.	40	77.88	22.12	16.84	4.01	1.27	2.59	16.18	99.34
" " Female.	41	79.20	20.80	17.65	1.95	1.20	2.76	17.24	99.59
" " Av. of 2 specimens.	..	78.54	21.46	17.24	2.98	1.24	2.68	16.71	99.47
Lake trout	17	68.78	31.22	17.32	12.55	1.35	2.82	17.62	100.30
"	255	69.50	30.50	19.12	10.21	1.17	2.97	18.52	100.30
" Average of 2 specimens	..	69.14	30.86	18.22	11.38	1.26	2.98	18.60	100.30
Brook trout	24	77.54	22.46	18.45	2.61	1.42	3.01	18.80	100.17
"	254	79.84	20.16	18.45	0.75	0.96	3.25	20.30	100.35
"	256	75.78	24.22	20.03	2.94	1.25	3.08	19.23	100.27
" Average of 3 specimens	100	77.72	22.28	18.97	2.10	1.21	2.96	18.43	100.26
Pickerel	224	79.84	20.16	18.40	0.52	1.24	3.04	19.02	100.03
"	..	79.52	20.48	18.88	0.49	1.11	3.00	18.73	100.14
" Average of 2 specimens	98	79.68	20.32	18.64	0.50	1.18	2.99	18.67	100.09
Pickerel, Pike.	45	79.79	20.21	18.60	0.58	1.03	3.22	20.15	100.07
Mascalonge.	4	76.26	23.74	19.63	2.54	1.57	3.08	19.25	100.52
Eel, salt-water.	217	69.80	30.20	18.95	10.34	0.91	2.84	17.75	100.30
"	126	73.40	26.60	17.61	7.88	1.11	2.96	18.50	100.14
" Average of 2 specimens	8	71.60	28.40	18.28	9.11	1.01	3.12	19.48	100.22
Mullet	13	74.87	25.13	19.32	4.64	1.17	2.92	18.29	100.16
Mackerel	30	78.67	21.33	18.13	2.20	1.00	2.80	17.51	100.16
"	39	74.26	25.74	17.48	7.02	1.24	2.91	18.18	100.03
"	230	74.14	25.86	17.57	6.99	1.30	3.05	19.08	100.61
"	261	64.01	35.99	18.21	16.30	1.48	3.12	19.46	100.87
"	..	73.68	26.32	19.25	5.86	1.21		19.43	100.21
"	..	75.44	24.56	19.07	4.21	1.28		18.63	100.36
" Average of 6 specimens	43	73.37	26.63	18.26	7.09	1.28	2.99		100.37
Spanish mackerel	234	68.10	31.90	20.97	9.43	1.50	3.43	21.45	100.48
Pompano	263	67.38	32.62	18.15	13.51	0.96	2.94	18.35	100.20
"	..	78.18	21.82	19.15	1.64	1.03	3.09	19.30	100.15
" Average of 2 specimens	12	72.78	27.22	18.65	7.57	1.00	3.02	18.83	100.18
Blue fish	90	78.46	21.54	19.02	1.25	1.27	3.11	19.41	100.39
Butter fish	53	70.02	29.98	17.81	11.03	1.14	2.88	17.99	100.18
Large-mouthed black bass	..	78.61	21.39	19.24	0.96	1.19	3.11	19.44	100.20

TABLE III.—Continued.

Kind of Fish	Laboratory Numbers of Specimens	Water	Water-free Substance	Albuminoids, etc. (by difference)	Fats, Ether Extract	Ash	Nitrogen	Protein, N × 6.25	Water + Protein + Fats + Ash
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Small-mouthed black bass	91	74.82	25.18	21.50	2.44	1.24	3.47	21.71	100.21
Yellow perch	127	80.43	19.57	17.88	0.55	1.14	2.85	17.79	99.91
"	208	78.07	21.93	19.47	1.12	1.34	3.15	19.69	100.22
" Average of 2 specimens		79.25	20.75	18.68	0.83	1.24	3.00	18.81	100.13
Pike perch, Wall-eyed pike	52	79.74	20.26	18.42	0.47	1.37	2.97	18.58	100.16
Pike perch, Gray pike	257	80.85	19.15	17.26	0.76	1.13	2.86	17.88	100.62
Striped bass	7	79.02	20.98	18.26	1.56	1.16	2.99	18.69	100.43
"	19	79.73	20.27	16.74	2.17	1.36	2.72	16.98	100.24
"	225	77.27	22.73	18.81	2.81	1.11	3.04	18.97	100.16
"	237	75.76	24.24	19.33	3.64	1.27	3.13	19.54	100.21
"	248	77.87	22.13	18.81	2.20	1.12	3.04	18.97	100.16
"	260	76.65	23.35	17.82	4.61	0.92	2.88	17.98	100.16
" Average of 6 specimens		77.71	22.29	18.30	2.83	1.16	2.93	18.53	100.23
White perch	44	75.64	24.36	17.63	5.62	1.11	2.87	17.95	100.32
"	46	75.77	24.23	20.43	2.52	1.28	3.29	20.58	100.15
" Average of 2 specimens		75.71	24.29	19.03	4.07	1.19	3.08	19.27	100.24
Sea bass	251	79.32	20.68	18.75	0.49	1.44	3.17	19.84	101.09
Grouper	114	79.95	20.05	18.51	0.38	1.16	2.98	18.68	100.17
"	271	78.96	21.04	19.19	0.71	1.14	3.17	19.81	100.62
" Average of 2 specimens		79.45	20.55	18.85	0.55	1.15	3.08	19.25	100.40
Red snapper	20	78.22	21.78	19.89	0.62	1.27	3.23	20.17	100.28
"	26	77.34	22.66	19.39	1.94	1.33	3.16	19.75	100.36
"	242	79.81	20.19	18.31	0.54	1.34	3.08	19.26	100.95
" Average of 3 specimens		78.46	21.54	19.20	1.03	1.31	3.16	19.73	100.53
Porgy	15	79.68	20.32	17.46	1.46	1.40	2.78	17.44	99.98
"	31	71.98	28.02	18.81	7.86	1.35	3.02	18.86	100.05
"	262	73.31	26.69	19.29	6.01	1.39	3.11	19.43	100.14
" Average of 3 specimens		74.99	25.01	18.52	5.11	1.38	2.97	18.58	100.06
Sheepshead	48	72.01	27.99	20.17	6.72	1.10	3.33	20.82	100.65
"	250	79.08	20.92	18.93	0.66	1.33	3.10	19.36	100.43
" Average of 2 specimens		75.55	24.45	19.54	3.69	1.22	3.22	20.08	100.54
Red bass	270	81.56	18.44	16.68	0.53	1.23	2.70	16.88	100.20
King fish	252	79.21	20.79	18.66	0.95	1.18	3.03	18.94	100.28

TABLE III.—Concluded.

Kind of Fish.	Laboratory Numbers of Specimens.	Water.	Water-free Substance.	Albuminoids, etc. (by difference).	Fats. Ether Extract.	Ash.	Nitrogen.	Protein, N × 6.25.	Water + Protein + Fats + Ash.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Weak fish,	273	78.97	21.03	17.45	2.39	1.19	2.85	17.80	100.35
Black fish,	38	76.95	23.05	18.96	2.81	1.28	3.09	19.33	100.37
"	205	81.36	18.64	17.44	0.55	0.65	2.82	17.61	100.17
"	244	79.64	20.36	18.71	0.62	1.03	3.03	18.91	100.20
"	269	78.44	21.56	18.76	1.44	1.36	3.03	18.96	100.24
" Average of 4 specimens,		79.10	20.90	18.47	1.35	1.08	2.99	18.71	100.24
Hake,	113	83.11	16.89	15.24	0.67	0.98	2.46	15.37	100.13
Cusk,	110	82.01	17.99	16.92	0.17	0.90	2.72	17.00	100.08
Haddock,	16	80.30	19.70	18.38	0.17	1.15	2.97	18.58	100.20
"	21	82.03	17.97	16.26	0.14	1.57	2.65	16.58	100.32
"	229	82.56	17.44	15.94	0.32	1.18	2.61	16.32	100.38
"	259	81.87	18.13	16.75	0.35	1.03	2.77	17.31	100.56
" Average of 4 specimens,		81.69	18.31	16.83	0.25	1.23	2.75	17.20	100.37
Cod,	3	83.48	16.52	14.97	0.28	1.27	2.48	15.49	100.52
"	11	83.39	16.61	14.95	0.40	1.26	2.58	16.09	101.14
"	206	80.71	19.29	17.59	0.30	1.40	2.93	18.32	100.73
"	228	83.43	16.57	15.26	0.31	1.00	2.54	15.84	100.58
"	243	82.20	17.80	16.08	0.51	1.21	2.69	16.80	100.72
" Average of 5 specimens,		82.64	17.36	15.77	0.36	1.23	2.54	16.51	100.74
Tom-cod,	99	81.55	18.45	17.08	0.38	0.99	2.76	17.24	100.16
Pollock,	81	76.02	23.98	21.65	0.78	1.55	3.46	21.60	99.95
Halibut,	1	79.15	20.85	17.49	2.21	1.15	2.80	17.53	100.04
"	9	70.13	29.87	18.16	10.57	1.14	2.97	18.54	100.38
"	211	76.97	23.03	19.40	2.75	0.88	3.15	19.68	100.28
" Average of 3 specimens,		75.42	24.58	18.35	5.17	1.06	2.97	18.58	100.23
Turbot,	49	71.39	28.61	12.93	14.41	1.28	2.36	14.75	101.83
Common flounder,	2	83.37	16.63	14.73	0.62	1.28	2.39	14.91	100.18
"	22	85.04	14.96	12.90	0.77	1.29	2.12	13.22	100.32
" Average of 2 specimens,		84.21	15.79	13.82	0.69	1.28	2.26	14.07	100.25
Winter flounder,	253	84.35	15.65	14.01	0.44	1.20	2.33	14.53	100.52
Lamprey eel,	236	71.12	28.88	14.93	13.29	0.66	2.40	14.98	100.05
Skate,	247	83.15	17.85	15.32	1.39	1.14	2.91	18.17	102.85

TABLE IV.

Sum of Protein ($N \times 6.25$), Ether Extract, Ash, and Water in Flesh of Specimens of American Fishes.

Laboratory Number.	NAME.	Protein + Ether Extract + Ash in Water-free Substance.	Protein + Ether Extract + Ash + Water in Flesh.
		per ct.	per ct.
40	Spent land-locked salmon.........	97.01	99.34
41	" " "	98.00	99.59
	" " " average	97.50	99.47
36	Spent salmon......... .... ·	99.15	99.82
35	" "	99.61	99.91
	" " average	99.38	99.87
81	Pollock......... .... ·	99.74	99.95
236	Lamprey eel.........	100.18	100.05
15	Porgy.. .... ·	99.94	99.98
31	"	100.16	100.05
262	"	100.57	100.14
	" average...	100.22	100.06
127	Yellow perch.........	99.55	99.91
208	" "	101.04	100.22
	" " average.........	100.29	100.13
110	Cusk.........	100.30	100.08
98	Pike pickerel.........	100.32	100.07
100	Pickerel......... ·	100.15	100.03
224	"	100.72	100.14
	" average.........	100.43	100.09
258	Small-mouthed red horse	100.48	100.09
111	Cisco.........	100.59	100.14
126	Mullet	100.61	100.16
90	Butter fish.........	100.62	100.18
234	Pompano	100.60	100.20
263	"	100.70	100.15
	" average.........	100.65	100.18
220	Alewife.........	100.70	100.18
5	" .... ·	100.77	100.20
	" average.........	100.73	100.19
113	Hake.	100.74	100.13
52	Pike perch, Wall-eyed pike	100.75	100.16
217	Salt-water eel.........	100.53	100.14
4	" " "	101.02	100.30
	" " " average...	100.77	100.22
91	Small-mouthed black bass.........	100.81	100.21
238	Sturgeon	100.81	100.15
99	Tom-cod.........	100.84	100.16
1	Halibut.........	100.18	100.04
211	"	101.19	100.28
9	"	101.30	100.38
	" average.........	100.89	100.23
221	Shad......	100.45	100.12
245	"	100.68	100.16
10	"	100.74	100.21
249	"	100.87	100.22
32	" .... ·	100.96	100.25
212	"	101.28	100.36
6	"	101.37	100.39
	" average.........	100.91	100.27

TABLE IV.—*Continued.*

Laboratory Number.	NAME.	Protein + Ether Extract + Ash in Water-free Substance.	Protein + Ether Extract + Ash + Water in Flesh.
		per ct.	per ct.
53	Large-mouthed black bass................................	100.92	100.20
46	White perch..	100.63	100.15
44	" "	101.32	100.32
	" " average....................................	100.97	100.24
17	Lake trout...	100.97	100.30
255	" "	101.01	100.30
	" " average....................................	100.99	100.30
260	Striped bass..	100.67	100.16
248	" "	100.73	100.16
225	" "	100.77	100.16
237	" "	100.88	100.21
19	" "	100.96	100.24
7	" "	102.03	100.43
	" " average....................................	101.00	100.23
269	Black fish..	100.93	100.20
205	"	100.95	100.17
244	"	100.98	100.20
38	"	101.62	100.37
	" average....................................	101.12	100.24
270	Red bass..	101.12	100.20
207	Smelt	99.17	99.82
23	"	103.09	100.62
	" average....................................	101.13	100.22
24	Brook trout..	100.75	100.17
256	" "	101.03	100.27
254	" "	101.72	100.35
	" " average....................................	101.17	100.26
252	King fish...	101.29	100.28
13	Mackerel..	100.15	100.03
8	"	100.73	100.16
230	"	100.94	100.21
261	"	101.46	100.36
30	"	102.37	100.61
39	"	102.39	100.87
	" average....................................	101.34	100.37
43	Spanish mackerel..	101.52	100.48
273	Weak fish..	101.64	100.35
2	Common flounder..	101.09	100.18
22	" "	102.19	100.32
	" " average....................................	101.64	100.25
233	California salmon..	101.67	100.60
12	Blue fish...	101.83	100.39
16	Haddock..	100.92	100.20
21	"	101.81	100.32
229	"	102.16	100.38
259	"	103.08	100.56
	" average....................................	101.99	100.37
114	Grouper	101.18	100.17
271	"	102.94	100.62
	" average....................................	102.06	100.40
47	Herring	102.07	100.66
280	Salmon	100.82	100.32

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TABLE IV.—*Continued.*

Laboratory Number.	NAME.	Protein + Ether Extract + Ash in Water-free Substance.	Protein + Ether Extract + Ash + Water in Flesh.
		per ct.	per ct.
14	Salmon..	101.10	100.46
279	"	101.27	100.49
78	"	103.08	101.07
77	"	104.43	101.62
	" average	102.14	100.79
45	Mascalonge..	102.20	100.52
250	Sheepshead...	102.08	100.43
48	"	102.33	100.65
	" average	102.20	100.54
20	Red snapper..	101.30	100.28
26	" "	101.69	100.36
242	" "	104.53	100.95
	" " average..............................	102.50	100.53
18	White fish...	102.87	100.87
257	Pike perch, Gray pike..	103.23	100.62
253	Winter flounder...	103.41	100.52
3	Cod..	103.03	100.52
228	"	103.55	100.58
206	"	103.76	100.73
243	"	104.22	100.72
11	"	106.87	101.14
	" average..	104.28	100.74
251	Sea bass..	105.04	101.09
49	Turbot...	106.39	101.83
247	Skate...	116.01	102.85
	PRESERVED FISH.		
79	Desiccated cod, flesh desiccated and ground, dried......	104.02	103.41
42	Mackerel, salted...	98.40	99.08
34	Salt cod, salted and dried.....................................	107.98	103.70
37	" " " "	109.06	104.19
	" " " " average.	108.57	103.95
88	Haddock, salted, smoked and dried............................	98.60	99.61
218	Halibut, " " "	100.03	100.01
28	" " " "	100.66	100.34
	" average..	100.35	100.18
33	Herring..	100.77	100.50
87	Sardines, canned...	98.99	99.56
94	Mackerel, canned...	99.13	99.72
95	Salt mackerel, canned	99.56	99.74
219	" " "	100.33	100.19
	" " " average...........................	99.95	99.97
29	Salmon, canned..	99.33	99.77
241	" "	100.65	100.27
96	" "	100.89	100.33
	" " average...	100.29	100.12
240	Tunny, "Horse mackerel," canned.............................	100.53	100.15
275	Smoked haddock, canned...	101.57	100.51

[*To be concluded in next number.*]

REVIEWS AND REPORTS.

The expression "chemical structure" as commonly used by chemists has, as is well known, nothing to do with the arrangement of atoms in space. The structural formula does not profess to represent spatial relations, but simply the connections which, after a careful study of the transformations and modes of formation of the compound represented, are believed to exist between the atoms. Nevertheless, although we do not commonly consider the question of space relations, it is clear that atoms must have some definite positions in the molecules, and the only reason why we do not represent these positions is because we know practically nothing about them. The most definite suggestion concerning space relations of atoms which has been made is that of Le Bel and Van't Hoff. The well known hypothesis of these authors was put forward to account for a certain kind of so-called physical isomerism which shows itself in the action of substances upon polarised light. Since this hypothesis was proposed, the number of cases of "abnormal isomerism," that is to say, of cases of isomerism which cannot be accounted for by the commonly accepted method of explaining structure, has increased to a considerable extent, and the necessity for some new hypothesis, or for some modification of the old ones, has come to be pretty generally recognised. Among the cases of isomerism which it is at least difficult to explain by the aid of the prevailing views are those of maleic and fumaric acids ; citraconic and mesaconic acids ; certain halogen derivatives of crotonic acid and of cinnamic acid ; and coumaric and coumarinic acids. More than one hypothesis has been proposed to account for these cases of isomerism, but no one has shown itself to be entirely satisfactory. Quite recently Johannes Wislicenus, Professor of Chemistry in the University of Leipsic, has made what has the appearance of being an important contribution towards the solution of the problem referred to. The author shows that many of the facts known in regard to the relations between maleic and fumaric acids, and the other substances which furnish examples of "abnormal isomerism," may be explained by the aid of an extension of the Le Bel–Van't Hoff hypothesis. It is difficult without the aid of models to give a clear idea concerning the hypothesis of Wislicenus, but some idea of it may be gained from the following. If we suppose a carbon atom to exert its affinities in the directions of the solid angles of a

tetrahedron, as is done in the Le Bel–Van't Hoff hypothesis, then, when two carbon atoms unite, as in ethane, the union will be between two solid angles of two tetrahedrons. If the two carbon atoms unite by the ethylene kind of union, the union will be along a line corresponding to one of the edges of each tetrahedron. In the former case, in which single union exists, the two parts of the molecule represented by the two tetrahedrons can be supposed to be capable of revolving around an axis either in the same direction or in opposite directions. This axis corresponds to the straight line joining the two carbon atoms. In the case in which double union exists no such revolution is possible. Again if, by addition to an unsaturated compound like ethylene, a saturated compound is formed, the kind of union between the carbon atoms is changed, and the possibility of revolution of the two parts of the compound is given. Whether such revolution take place or not will be determined largely by the structure of the compound. The tendency will be for those parts of the molecule which have the greatest specific affinity for one another to take those positions in which they are nearest to one another. Thus, suppose that chlorine is added to ethylene. By following the change on the model, it is seen that in the resulting figure the two chlorine atoms in ethylene chloride are situated at angles of the two tetrahedrons which are nearest each other. But chlorine has a stronger affinity for hydrogen than it has for chlorine, and therefore each chlorine atom would tend to get as near a hydrogen atom as possible. This involves a partial revolution of the two tetrahedrons in opposite directions around their common axis. So also hydrogen would tend to take a position as near as possible to hydroxyl and to carboxyl, while hydroxyl would avoid hydroxyl, and carboxyl would avoid carboxyl. These views are suggested as a result of a careful application of the original Le Bel–Van't Hoff hypothesis, and are, of course, of little value unless they can be shown to be in accordance with the facts.

The chief merit of the work of Wislicenus consists in the fact that he has shown that a large number of phenomena which have been observed in the study of such cases of isomerism as were mentioned above, find a ready explanation in terms of the new hypothesis, whereas for most of these phenomena no explanation whatever has thus far been presented. The most marked case presented is that of maleic and fumaric acids. One by one the author discusses the transformations of these acids and their substitution products, and he comes to this conclusion: "There is not to my knowledge a single fact known in regard to the relations between fumaric and maleic acids which is not explained by the aid of the above geometrical considerations, not one which does not clearly support the new hypothesis." Among the facts which he discusses in the light of the hypothesis are these: The formation of fumaric and maleic acids from malic acid; the quantitative transformation of maleic into fumaric acid by contact with strong acids;

the transformation of the ethereal salts of maleic acid into those of fumaric acid by the action of a minute quantity of free iodine; the formation of brommaleic acid and hydrobromic acid from the dibromsuccinic acid formed by the addition of two bromine atoms to fumaric acid; the formation of dibromsuccinic acid from brommaleic acid, and of isodibromsuccinic acid from bromfumaric acid by the action of fuming hydrobromic acid; the conversion of brommaleic acid into fumaric and then into succinic acid by the action of sodium amalgam; the formation of one and the same tribromsuccinic acid by the action of bromine on brommaleic and on bromfumaric acid; and finally, the conversion of maleic into inactive tartaric acid, and of fumaric into racemic acid by potassium permanganate. All these facts are shown to find a ready explanation by the aid of the new hypothesis. Further, it is shown that the decompositions of the salts of certain halogen derivatives of organic acids, which give up halogen salt and carbon dioxide, as well as the formation of lactones and of anhydrides of dibasic acids, are in perfect harmony with the hypothesis. But the only way to get a clear conception in regard to the mass of material which the author has brought together and which he has shown to support his hypothesis is by a careful study of the original paper, and the object of this notice is mainly to call the attention of American chemists to it.

As to the question what value to attach to the speculations which Wislicenus has brought to our notice it is difficult to give any but a general answer. No one can well have a greater fear of mere speculation, which is indulged in independently of the facts, than the writer of this notice. Great harm has been done chemistry, and probably every other branch of knowledge, by unwarranted speculation, and every one who has looked into the matter knows how extremely difficult it is to emancipate one's self from the influence of a plausible hypothesis even when it can be shown that it is not in accordance with the facts. It behooves every one, therefore, before accepting a new hypothesis, no matter how fascinating it may appear at first sight, to look carefully into the facts, and to endeavor to determine independently whether it is well founded or not. On the other hand, there is some danger to be apprehended from a tendency, sometimes observed, to denounce everything speculative, no matter how broad the basis of facts upon which it rests may be. Without legitimate speculation it is clear that there could be no great progress in any subject. As far as the hypothesis under consideration is concerned, the writer is firmly of the opinion that it is likely to prove of great value in dealing with a large number of chemical facts, and that, as it suggests many lines of research, it will undoubtedly in the course of a few years exert a profound influence on chemistry. Whether the evidence which will be accumulated will or will not confirm the view that the tetrahedron form is characteristic of the simplest molecules of carbon

compounds is not the most important question to be asked under the circumstances. We should rather ask whether the testing of the hypothesis is or is not likely to bring us nearer to the truth. It is a proposition that admits of no denial that a hypothesis which can be tested by experiment, and which suggests lines of work and stimulates workers to follow them, is a gain to science no matter what the ultimate fate of the hypothesis may be.

PRINCIPIEN DER ORGANISCHEN CHEMIE. Von Dr. Eugen Lellmann, Privat-docent der Chemie an der Universität Tübingen. Berlin: Verlag von Robert Oppenheim, 1887. 511 pp. 8vo.

The author of this book has brought together all reactions of carbon compounds which have anything like a general character and treated them systematically. The book is intended not as a text-book of organic chemistry, but rather as a supplement to the larger books on this subject, the object being especially to emphasise the synthetical reactions and to point out the relations between these reactions, and the generalisations which the facts now in our possession justify. No similar attempt has been previously made, so that the author has had to rely entirely upon his own ingenuity in classifying the reactions. In his treatment they fall under four heads: I. Reactions in which the number of carbon atoms in a compound is not changed; II. Building up of a compound with a larger number of carbon atoms from such as contain a smaller number; III. Decomposition of a compound into several others, each of which contains a smaller number of carbon atoms; and IV. Action of two carbon compounds upon each other, resulting in the formation of two new organic substances. Under I the following sub-classes of reactions are treated: (1) Molecular re-arrangements; (2) Addition of elements or inorganic compounds to organic compounds; (3) Splitting off of elements or inorganic compounds from organic compounds; (4) Substitution phenomena. Under II are the following: (1) Addition of two organic compounds to each other; (2) Addition of two organic compounds to each other accompanied by the taking up of an element; (3) Separation of the constituents of an inorganic compound from several organic compounds and union of the organic residues; (4) Separation of constituents from several organic compounds caused by the action of elements, and union of the organic residues. Under III there are taken up: (1) Simple decomposition of an organic compound into several others; (2) Decomposition of an organic compound into several others preceded by the taking up an element or of the constituents of an inorganic compound.

The book is enriched by references to the important sources of information down to January 1, 1885, and later articles which

appeared while the book was passing through the press have also been considered as far as possible. It is clearly written, and will be of assistance in helping students to take a broad view of the chemical changes with which they are constantly dealing. In the usual method of treatment the individual reactions are necessarily kept in the foreground, and interesting and important generalisations are to a great extent lost sight of; indeed, it is only after one has acquired a pretty thorough knowledge of the various reactions met with that generalisations in regard to them have any significance. Advanced students are earnestly advised to study Dr. Lellmann's book with care.

THE PRINCIPLES OF THEORETICAL CHEMISTRY, WITH SPECIAL REFERENCE TO THE CONSTITUTION OF CHEMICAL COMPOUNDS. By Ira Remsen. Third edition, enlarged and thoroughly revised. Philadelphia : Lea Brothers & Co., 1887. 318 pp. 12mo.

This book has been enlarged from 242 to 318 pages, and has also been rewritten to a large extent. In the preface the author says : " The chapter on valence has been almost entirely rewritten and at the same time enlarged, and I feel that the treatment of the subject is now much more satisfactory than in the earlier editions. A brief introductory chapter, and chapters on matters pertaining to the subject of chemical affinity, and the connection between constitution and chemical conduct, have been added, and many other additions have been made throughout the book.

" The treatment of the subject of chemical affinity and allied subjects is purposely as brief and simple as possible, the object being mainly to interest the student, in the field of which but a glimpse is given, and to give a general idea of the results which have recently been reached."

DIE KÜNSTLICHEN ORGANISCHEN FARBSTOFFE. Unter Zugrundelegung von sechs Vorlesungen, gehalten von Prof. Dr. E. Noelting, Director der "École de Chimie" in Mühlhausen, bearbeitet von Dr. Paul Julius. Berlin : R. Gaertner, 1887. 235 pp.

The number of organic dye-stuffs is increasing so rapidly that it is almost impossible for one to keep thoroughly informed, even in regard to those which are described in scientific journals. But in addition many others are constantly being made and patented, and not described in the regular journals. Information in regard to the latter can usually be obtained only from the descriptions of patents in the different countries. The need of a connected treatise on these compounds is obvious, and recently two small books have appeared having the organic dye-stuffs as their subject. The book before us is admirably arranged, and

gives in a small space a clear treatment of the many dye-stuffs and the relations existing between them. The first chapter treats of coal tar and the chemistry of benzene and its derivatives. The second, of the intermediate products in the preparation of dye stuffs. These are the derivatives of the hydrocarbons which must be made in order to get the dye-stuffs themselves, as, for example, nitrobenzene, aniline, toluidine, phthalic acid, benzoic aldehyde, resorcin, pyrogallol, etc. The theory in regard to the cause of the coloring properties of certain organic compounds is next considered, and then in succeeding chapters the most important dye-stuffs are taken up.

RECENT ADVANCES IN THE CHEMISTRY OF MANGANESE, AND A NEW DE-
TERMINATION OF THE ATOMIC WEIGHT OF FLUORINE.

Up to the present time, five oxides of manganese have been known: Manganous oxide, MnO; red manganese oxide, Mn_2O_4; manganic oxide, Mn_2O_3; manganese dioxide, MnO_2; and manganese heptoxide, Mn_2O_7. From some recent investigations which have been carried on by Franke,[1] it appears that two new members must now be added to this list.

Manganese trioxide, MnO_3.—When potassium permanganate is added to well-cooled concentrated sulphuric acid it dissolves with a beautiful green color, and if to this cool solution either an excess of the permanganate or a small quantity of water be added, a heavy liquid of a metallic lustre separates, which Aschoff has shown to be the heptoxide of manganese, Mn_2O_7. On the other hand, when this green solution to which a small quantity of water has been added is warmed cautiously to 40°–50°, a *beautiful violet-colored gas* is evolved, which Franke has found to have the composition MnO_3.

The action of the sulphuric acid on potassium permanganate he believes can be rightly expressed by the following equations:

I. $2KOMnO_3 + H_2SO_4 = K_2SO_4 + 2OH.MnO_3$.

II. $2OH.MnO_3 + H_2SO_4 = (MnO_3)_2.SO_4 + H_2O$.

Kept cold: $(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4$.

Warmed to 30°: $(MnO_3)_2SO_4 + H_2O = 2MnO_3 + H_2SO_4 + O$.
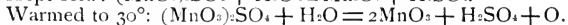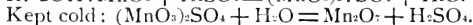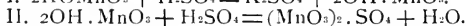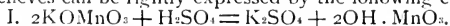
The oxysulphate of manganese, $(MnO_3)_2SO_4$, which he regards as the intermediate product in these reactions, has not been shown to exist in the sulphuric acid solution of potassium permanganate, though some strictly analogous compounds are known. These are the manganese oxychloride of Aschoff, MnO_3Cl, and the manganese oxyfluoride of Wöhler, MnO_3F; so that it is safe to assume the existence of a corresponding oxysulphate. A still more convenient method of preparation, and one by which the gas can be obtained in larger quantities and purer condition, consists in treating the oxysulphate solution with potassium carbonate:

$$(MnO_3)_2SO_4 + K_2CO_3 = 2MnO_3 + K_2SO_4 + CO_2 + O.$$
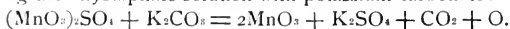
[1] Journal für praktische Chemie **36**, 31.

20 cc. of the oxysulphate solution, which is best made by dissolving 5 to 8 grams of potassium permanganate in concentrated sulphuric acid, is allowed to flow drop by drop into a small flask containing 10 grams of dry potassium carbonate. The gases evolved in this reaction are conducted through a U-tube, which is surrounded by a freezing mixture. The oxide thus obtained, and which at ordinary temperatures is a violet-colored gas, condenses in the U-tube to a dark red, amorphous mass. It has a peculiar odor, and attacks the mucous membranes of the throat and nose, producing a cough. When heated gradually to 50° C. the dark red amorphous mass is transformed into a violet-colored vapor with partial decomposition into manganese dioxide and oxygen. When heated suddenly or to a temperature higher than 50° C. it breaks down completely into manganese dioxide and oxygen. It dissolves with difficulty in water, and this solution is found to contain free manganic acid; this, however, soon decomposes, manganese dioxide and oxygen are set free, and a new acid, dimanganic acid, is formed. This probably has the composition and structure represented by the formula $O{<}{MnO_2.OH \atop MnO_2.OH}$. When the violet gas is conducted into solutions of caustic potash or soda it dissolves with a green color, and the manganates of these metals are formed. Conducted into sulphuric acid, the acid becomes yellow, and if the operation be continued, manganese dioxide separates and a green solution of the oxysulphate is formed. This trioxide, MnO_3, is an exceedingly powerful oxidising agent; it oxidises hydrochloric acid, as do the other oxides of manganese, with the formation of chlorine. The new oxide possesses a remarkable coloring power, 0.0050 gram of the substance being sufficient to cover the inside of a litre flask with an intense red color.

Manganese tetroxide, MnO_4.—When moist carbon dioxide gas is conducted over the oxysulphate solution there is formed, in addition to the oxide just described, a quantity of a blue gas, which Franke believes to be the tetroxide of manganese, MnO_4. This blue gas is condensed by cold to a bluish-violet amorphous substance which is more volatile than the trioxide MnO_3. It dissolves in water less readily than the trioxide, and differs from it in other ways. Up to the present, such small quantities of this substance have been obtained that it has been impossible to determine its composition by analysis. Nevertheless, the properties and reactions of the substance point to the formula MnO_4, and the formation of the tetroxide from the oxysulphate solution is probably to be represented in this way:

$$\frac{MnO_3}{MnO_3}{>}SO_4 + H_2O = MnO_4 + MnO_3 + H_2SO_4.$$
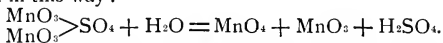
The Higher Chlorides of Manganese.—Nicklès[1] was the first to study the action of dry hydrochloric acid gas on manganese dioxide in the presence of anhydrous ether, and he came to the

[1] Annales de Chim. et de Phys. [4], 5, 161.

conclusion that manganese tetrachloride is formed in this way, and that this combines with the ether and with the water formed during the reaction to form a violet-colored compound of the formula $MnCl_4 + 12(C_2H_5)_2O + 2H_2O$. Christensen[1] has recently taken up the study of the action of dry hydrochloric acid on manganese dioxide and manganic oxide, Mn_2O_3, in the presence of ether, and has reached results differing considerably from those of Nicklès. He does not attempt the complete analysis of the compounds formed, as they cannot be obtained in pure condition; but, by determining the relation between the quantity of *active chlorine* and manganese in these compounds, he is led to more correct views regarding their composition. In manganese tetrachloride, $MnCl_4$, for example, the atomic ratio between the manganese and the *active chlorine* is $1 : 2$, whereas in manganic chloride, Mn_2Cl_6, the ratio is $11 : 1$. This ratio can be determined approximately even in the presence of an excess of hydrochloric acid or of organic compounds containing chlorine. The results are briefly these : When dry hydrochloric acid acts on manganese dioxide and manganic oxide in the presence of ether, at ordinary temperatures, the compound formed is the same in both cases, and the ratio between the manganese and active chlorine corresponds to that required by the formula Mn_2Cl_6, that is, as $1 : 1$. At low temperatures ($-10°$) manganese tetrachloride seems to be the main product of the reaction. When the ether contains but a small quantity of hydrochloric acid a blue solution is formed, which becomes green on the addition of more hydrochloric acid. Christensen supposes this change of color to be due to the formation of a hydrated salt from one containing no water, and that there are two chlorides of manganese, viz. Mn_2Cl_6 and $Mn_2Cl_6 + xH_2O$, which correspond to the analogous chromic chlorides, Cr_2Cl_6 and $Cr_2Cl_6 + 12H_2O$.

Franke[2] claims that this explanation of the change in color is not supported by facts, and shows that the blue solution contains manganese tetrachloride, which changes into the green compound by taking up hydrochloric acid directly, forming the compound $\dfrac{HCl}{HCl} > MnCl_4$. In other respects Franke's work confirms the results obtained by Christensen.

Compounds of Manganese and Fluorine.—Christensen has also been engaged of late in studying the action of hydrofluoric acid on the oxides and hydroxides of manganese.

Manganic fluoride, $Mn_2F_6 + 6H_2O$.—When pure manganese dioxide is treated with hydrofluoric acid this compound is formed. It crystallises in dark brown prisms. It can also be formed by dissolving manganite, H_2MnO_4, in hydrofluoric acid. When manganic fluoride is treated with a concentrated solution of potassium fluoride, a beautiful rose-red double salt of the composition $4KF . Mn_2F_6 + 2H_2O$ crystallises out. The salt can be more easily prepared by fusing acid potassium fluoride, $HF.KF$, with man-

ganese dioxide. This salt was prepared some time ago by Nicklès, who assigned to it the formula $2KF.MnF_4$, and considered it as a salt of the acid H_2MnF_6, which he regarded as the analogue of hydrofluosilicic acid. This view, according to Christensen, is untenable, and we must, according to him, regard the salt as analogous to certain double fluorides and chlorides which occur in nature. These belong to the general type $4RF.M_2F_6$; and all of Christensen's experiments tend to show that *manganic oxide*, Mn_2O_3, *is strictly analogous to the corresponding oxides of aluminium and iron.*

The corresponding double salt of manganese and ammonium, $4NH_4F.Mn_2F_6$, can be easily prepared in pure condition, and has been used by Christensen in the redetermination of the atomic weight of fluorine. These determinations are based upon the determination of *active fluorine* in the compound, and his best · results give as the atomic weight of fluorine, 18.91, 18.94, 18.95, 18.91 and 18.94 respectively. For $H = 1$ the atomic weight of fluorine is therefore 18.94. For $O = 16$ we have $F = 18.99$, or very nearly 19.0. J. H. K.

NOTES.

The Constitution of Selenious Acid.

In nearly all the attempts that have recently been made to determine the constitution of inorganic compounds, the organic derivatives of these compounds have generally played an important part. Thus the constitution of the platinum bases was determined by Jörgensen by introducing pyridine in the place of ammonia; phosphorus was shown to be pentavalent by La Coste and Michaelis, who prepared the isomeric compounds $(C_6H_5)_3PO$ and $(C_6H_5)_2P(OC_6H_5)$; triphenyl bismuth bromide, $(C_6H_5)_3BiBr_2$, prepared by Polis and Michaelis, proved bismuth to be also pentavalent. Particularly in the investigations on the constitution of the inorganic acids, such as phosphorous and sulphurous acids, have the organic derivatives been used.

It is now pretty well settled that the hypothetical sulphurous acid obtained from the sulphites is the so-called unsymmetrical acid $H.SO_2.OH$, and not the normal or symmetrical dihydroxyl acid $SO(OH)_2$. This has been shown, on the one hand, by the fact that the alkyl iodides and alkali sulphites react to form salts

of alkyl sulphonic acid, in which the alkyl residue is undoubtedly connected with the sulphur—

$$K_2SO_3 + C_2H_5I = C_2H_5SO_3K + KI,$$

and, on the other hand, by the formation of the ethyl salt of ethyl-sulphuric acid by the action of ethyl iodide upon silver sulphite,

$$Ag_2SO_3 + 2C_2H_5I = C_2H_5SO_2OC_2H_5 + 2AgI;$$

while, by the action of alcohol on thioxyl chloride, the ethyl salt of sulphurous acid, $(C_2H_5O)_2SO$, isomeric with the preceding, is formed—

$$SOCl_2 + 2C_2H_5OH = SO(OC_2H_5)_2 + 2HCl.$$

Michaelis and Landmann[1] now take up the question of the constitution of selenious acid, and find that it must be regarded as having a constitution entirely different from that of sulphurous acid, and that it is a true dihydroxyl acid, $SeO(OH)_2$. This they show by the fact that potassium selenite conducts itself toward ethyl iodide in an entirely different manner from potassium sulphite. Instead of a salt corresponding to an alkyl sulphonic acid being formed, all the selenium is precipitated in the free state. The ethereal salts made, on the one hand, from ethyl iodide and silver selenite,

$$2C_2H_5I + Ag_2SeO_3 = (C_2H_5O)_2SeO + 2AgI,$$
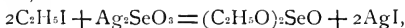
and, on the other, from sodium ethylate and selenyl chloride,

$$2C_2H_5ONa + SeOCl_2 = 2NaCl + SeO(OC_2H_5)_2,$$
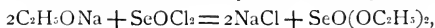
were then compared and found to be identical in every respect. It hence follows that the ethereal salt made in both ways has the same constitution, $SeO(OC_2H_5)_2$. The selenites have accordingly the constitution $SeO(OM)_2$, and selenious acid is a true dihydroxyl acid, $SeO{<}^{OH}_{OH}$, and in this respect differs markedly from sulphurous acid. W. R. O.

Professor Wolcott Gibbs has resigned the Rumford Professorship in Harvard University in order to devote himself exclusively to research. He has removed to Newport, R. I., where he is erecting a private laboratory.

[1] Annalen der Chemie **241**, 150.

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